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Monohydric Alcohols

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Monohydric Alcohols

Manufacture, Applications, and Chemistry

Edward J. Wickson, Editor
Exxon Chemical Company

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FOREWORD

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PREFACE

Unsubstituted monohydric alcohols are the largest single class of oxygenated hydrocarbons made in the chemical industry. In fact, three of the alcohols—methanol, ethanol, and isopropyl alcohol—are in *Chemical and Engineering News* "Top 50 Chemicals" for 1979. These alcohols are used in a myriad of applications, some very large and others quite small. Solvents, fuels, antifreeze, germicides, frothers, antifoams, and inks are examples of where the alcohols are used as such. Derivatives cover an even wider range of applications, including resins, solvents, plasticizers, surfactants, lubricants, flavors, fragrances, capacitor fluids, and the fast growing gasoline additive MTBE, to name a few. In this sense, alcohols differ markedly from some of the very large volume organics such as ethylene, propylene, toluene, *p*-xylene, and urea, which are used in very large volumes but have relatively few end uses.

It is common practice to divide alcohols into lower alcohols (C_1–C_5) and higher alcohols (C_6 and higher). In turn, higher alcohols are generally subdivided into (polyvinyl chloride) plasticizer range (C_6–C_{11} or C_6–C_{12}) and detergent range (C_{11} or C_{12} and higher). Actually, the dividing line is not this clear cut, and one finds the lower alcohol *n*-butanol used in butyl benzyl phthalate and the detergent-range tridecyl alcohol used in ditridecyl phthalate. Both of these esters are important polyvinyl chloride plasticizers. Also, detergents based on mixed alcohols, including C_{11}, are produced commercially, and there are many surfactants, such as di-2-ethylhexyl sulfosuccinate, based on the so-called plasticizer-range alcohols.

In developing the symposium on which this book is based, our objective was not to cover all monohydric alcohols, but to cover representative lower and higher alcohols with special attention, when possible, to new developments and applications.

The book starts with a review of the chemistry of monohydric alcohols with references to many of the common reactions used in industry.

Much attention has been devoted in the professional journals and in the press to gasohol, and announcements of new ethanol plants and process improvements seem unending. A perspective on the problems and promise of gasohol is covered along with a status report on work in Brazil on (fuel) methanol from wood, not by destructive distillation used in the past, but by modern synthetic chemistry. Other promising new uses for

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methanol are covered that together suggest enormous growth for this first member of the monohydric alcohol series.

A detailed discussion on surfactants from secondary alcohols which are relatively little known in the U.S. is included, together with a review of linear alcohol processes (Oxo and Ziegler) and detergent applications of the Ziegler alcohols. Also covered is a discussion of the revolutionary rhodium oxo process which has already resulted in a number of new plants—announced, under construction, or in operation, worldwide—for the manufacture of *n*-butanol and 2-ethylhexanol. Applications of these alcohols are also discussed.

The application of branched-chain alcohol diesters in part-synthetic lubricants is covered as one of the ways the petroleum industry is responding to the challenges brought on by the trend toward new smaller cars with more demanding lubricant requirements.

The history of monohydric alcohol–based ester-type plasticizers for polyvinyl chloride is reviewed, and a prediction of the future for these plasticizers in the eighties is made. Finally, although not in the large volume category compared to many monohydric alcohols, the rather sophisticated chemistry used to produce monohydric alcohols for the flavors and fragrance industry is covered.

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Chemistry of Monohydric Alcohols

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Alcohols can be regarded as hydroxyl derivatives of hydrocarbons. They can be characterized by the number of hydroxyl groups (monohydric, dihydric, etc.), according to their structure (primary, secondary or tertiary), and by the structure of the hydrocarbon function to which the hydroxyl is attached (aliphatic, cyclic, saturated or unsaturated).

This chapter is concerned almost exclusively with the chemistry of saturated aliphatic monohydric alcohols with particular emphasis on the reactions used in the conversion of these alcohols to other useful compounds. Manufacture of many of the alcohols is covered in other chapters.

Acidity and Basicity

Alcohols are amphoteric and thus can function both as weak Brønsted acids and as bases:

$$R\text{-}OH + Z^{\ominus} \rightleftharpoons R\text{-}O^{\ominus} + ZH \quad \text{(ROH acting as an acid)}$$

$$R\text{-}OH + HA \rightleftharpoons ROH_2^{\oplus} + A^{\ominus} \quad \text{(ROH acting as a base)}$$

The acidity of the hydroxyl group can be seen in the rapid proton-deuteron exchange that can take place when alcohols are dissolved in D_2O (Reaction I), alkali metals (Reaction II) and organometallic reagents (Reaction III and IV).

$$CH_3CH_2OH + D_2O \rightleftharpoons CH_3CH_2OD + DOH \qquad (I)$$

$$CH_3OH + Na \longrightarrow CH_3O^{\ominus}Na^{\oplus} + 1/2\ H_2 \qquad (II)$$

$$CH_3CH_2CH_2OH + CH_3Li \longrightarrow CH_3CH_2CH_2O^{\ominus}Li^{\oplus} + CH_4 \qquad (III)$$

$$CH_3CH_2CH_2OH + C_3H_7MgBr \longrightarrow CH_3CH_2CH_2O^{\ominus}MgBr^{\oplus} + C_3H_8 \qquad (IV)$$

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The most complete measurements of the acidity of alcohols in water were made some time ago by Long and Ballinger (1,2,3) using conductivity methods. The pKa values for substituted methanols (RCH_2OH) (2) are a linear function of the Taft σ* constants (4,5) for the R substituents, allowing the prediction of the actual pKa by using the formula: pKa = 15.9 - 1.42 σ*.

In recent years the question of acidity and basicity has been reopened by the development of techniques to measure them in the gas phase(6). The results available reemphasize the fact that solvation factors have a profound influence on the course of acid-base reactions.

Brauman and Blair have determined (6) that the acidity of some substituted alcohols increases as the size and number of substituents increase. This is exactly the opposite effect seen in solution measurements. The conclusion that must be deduced from this is that there are two kinds of acidity that must not be confused: a) an intrinsic acidity, which is best approximated by gas-phase measurements and which reflects the properties of the ions and the molecules in isolation, and (b) a practical liquid phase acidity in which solvation effects play a very important role. In the interpretation of structure-acidity relationships in solvents, the results will probably be misleading unless the structures being compared are very similar.

Categories of Chemical Reactions of Alcohols

The following sections on the chemical reactions of alcohols has been broken down into five categories: (A) Nucleophilic reactions of alcohols, (B) displacement of the hydroxyl group, (C) dehydration of alcohols, (D) oxidation of alcohols, and (E) analytical determination of the hydroxyl group.

Under each one of these categories the different types of reactions are organized in a logical manner. Some examples are given, but by no means are all the different types of alcohols covered. The reader is asked to extend the analogies and use the references given to pursue his areas of interest.

Nucleophilic Reactions

Any species having an unshared pair of electrons may act as a nucleophile, whether it is neutral like an alcohol or negative like the alkoxide ion. The rate of S_N1 reactions is independent of the structure and charge of the nucleophile. For S_N2 reactions, factors like the charge of the nucleophile, its degree of solvation and nucleophilicity determine the rate of the reaction (6A).

The major trend in nucleophilicity is to parallel base strength. However, sometimes differences between basicity and nucleophilicity of a species occur because the two are somewhat different. Basicity measures attack on hydrogen and it is

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thermodynamically controlled. Nucleophilicity on the other hand measures attack on carbon and it is kinetically controlled.

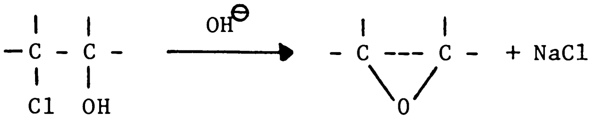
Reactions of the Alkoxide Ion. The nucleophilic reactions of the alkoxide ion (RO^-) are very similar to those of the hydroxide ion (OH^-) with the exception that the latter has an extra ionizable proton which can lead to further reaction after the initial nucleophilic attack.

The displacement of the bromide ion from an alkyl bromide (Reaction V) by an alkoxide has been found to be a first order reaction in both the reactant and substrate (7). It is implicit

$$RO^{\ominus} + R'\text{-}Br \longrightarrow ROR' + Br^{\ominus} \qquad (V)$$

in the reaction above that inversion of configuration will take place at the alkyl halide. The nucleophilic displacement of a halide by an alkoxide is commonly known as the Williamson ether synthesis and is still the best general method for the preparation of symmetrical and unsymmetrical ethers (7A).

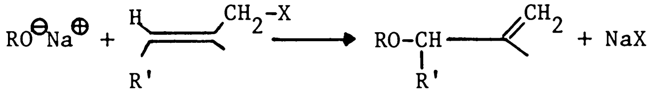
The transformation of chlorohydrins into the corresponding epoxides (Reaction VI) may be regarded as a special case of the Williamson reaction. Many epoxides have been made this way



(VI)

and the method is generally useful for the synthesis of five and six-membered rings. There is a large amount of evidence for an intramolecular mechanism (8).

When the halide is bonded to an allylic system (CH_2=CH-CH_2-X) an alkoxide ion will react analogously to the previously described S_N2 displacement on an alkyl halide. The most significant difference is the rate enhancing effect of the alkene moiety which has been attributed to a decrease in the activation energy of the reaction (9). A second possible mode of reaction is available with allylic halides. This mode of displacement is usually called S_N2' and, in general, will be promoted relative to the normal displacement when there are substituents on the alpha carbon which tend to inhibit the normal S_N2 pathway by inductive or steric effects (Reaction VII).



(VII)

Thus, while alpha-methylallyl chloride yields only a small amount of "abnormal" product with ethoxide ion in ethanol (10),

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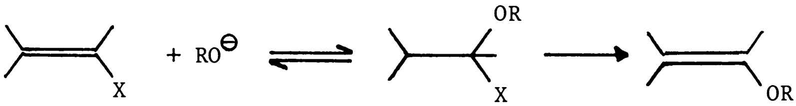
tert-butylallyl chloride forms substantial amounts of "abnormal" product derived through the S_N2' pathway (11).

The high electron density in the double bond system of ethylenes makes nucleophilic attack unfavorable unless the system is substituted with one or more electron withdrawing groups such as $-NO_2$, -CN, -COR. When these substituents are present, attack by alcohols or alkoxide ions occurs at the beta-carbon predominantly. For example, researchers have found (12) that sodium methoxide or sodium ethoxide added rapidly at room temperature to beta-nitrostyrene leads to the alkoxide formation of the derivative (Reaction VIII). This reaction is generally not only for arylnitroalkenes (13) but also for other activated double bonds (14). Another example of alcohol addition to an activated double bond includes the reaction of alcohols with acrylonitrile to produce a cyano-ethylated ether (14A).

$$C_6H_5CH{=}CHNO_2 + RO^{\ominus} \longrightarrow C_6H_5\underset{\displaystyle OR}{\underset{|}{C}}H{-}CH_2{-}NO_2 \qquad \text{(VIII)}$$

If there is a labile substituent directly attached to the double bond, a substitution reaction can occur after the initial attack by the anion (Reaction IX). There are several mechanisms

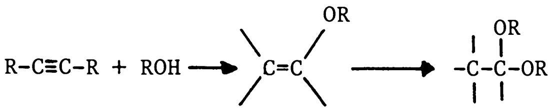


(IX)

which can account for the product formed, the most important of these is the "elimination-addition" mechanism in which an intermediate acetylene is initially formed which then adds an alcohol.

In general, the "addition-elimination" mechanism will be favored for compounds with low electron density on the beta-carbon, while the "elimination-addition" pathway will be favored by cis-isomers where there is a good chance of eliminating the elements of HX from a trans-position.

Addition to Acetylenes. Since triple bonds are more susceptible to nucleophilic attack than double bonds, it might be expected that bases would catalyze additions particularly well. This is the case, and vinyl ethers as well as acetals may be produced by the reaction of acetylenes with alcohols (15,15A) (Reaction X).



(X)

As with alkenes, the addition of alcohols to acetylenes is facilitated by the presence of electron-withdrawing substituents

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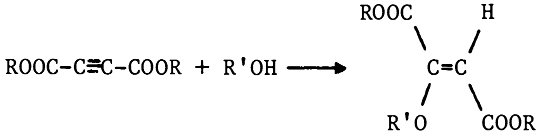
and is believed to proceed by a trans-mechanism(16). Thus, addition of alcohols to an acetylene dicarboxylate gives mainly the trans-compound (Reaction XI); some exceptions occur at high temperatures and with dicyanoacetylenes where the cis-isomer is sometimes produced.



(XI)

Because of the high electron density of the aromatic systems, nucleophilic aromatic substitutions usually occur only where the ring is substituted with one or more electron-withdrawing groups ortho and/or para to the position of substitution.

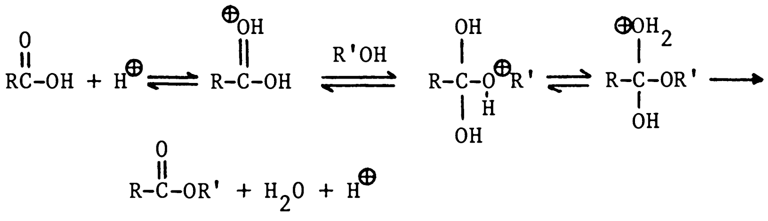
In general, the reactions are second-order, first-order with respect to both nucleophile and substrate (17). The relative activating effects of various substituents have been determined (18) to be in the order:

$$-N_2^{\oplus} > -NO_2 > -SO_2CH_3 > -\overset{\oplus}{N}(CH_3)_3 > -CN > CF_3$$

Esterification. Without a doubt, the best known nucleophilic reaction of alcohols is the reaction with organic acids and some derivatives, like acid anhydrides and acid chlorides, to form esters (Reaction XII).

$$RCO_2H + R'OH \xrightarrow{H^{\oplus}} RCO_2R' + H_2O \qquad \text{(XII)}$$

Esterification is an acid catalyzed reversible reaction which is known to proceed according to the following mechanism:



The best catalysts for this reaction are inorganic acids (H_2SO_4, HCl), organic acids (p-toluenesulfonic, methanesulfonic) and metal compounds such as tin and titanium derivatives - e.g. tetraisopropyl titanate. To achieve good yields of products, not only is a catalyst generally necessary but also the means to drive the equilibrium to the right as written in the reactions above.

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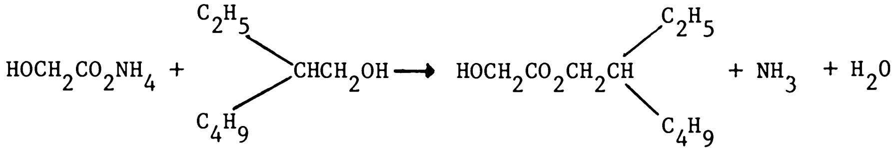
There are many ways of changing the equilibrium, among which are: (a) The addition of an excess of a reactant, (b) the removal of the ester or more commonly the water by distillation using an azeotroping agent, and (c) the removal of water by a dehydrating agent. An example is the commercial preparation of ethyl acetate from an aqueous solution of ethanol, acetic acid and sulfuric acid. It happens that the lowest-boiling liquid is a ternary mixture of ethyl acetate (83.2%), ethanol (9%), and water (7.8%). In the final steps of the process the ethanol is removed by washing with water. Many of the simpler esters can be made in this way.

The necessity for the continuous removal of water can be avoided by operating in a system composed of an aqueous and a non-aqueous layer. When a mixture of adipic acid, methanol, sulfuric acid, and ethylene chloride is heated, dimethyl adipate passes into the ethylene chloride layer; the lower layer contains the water (19).

Esters can also be made in satisfactory yields by heating an alcohol with the ammonium salt of an acid under conditions permitting removal of both ammonia and water from the reaction mixture. The method is general and is especially recommended where acid conditions are deleterious to the reactants. An example is the synthesis of 2-ethylhexyl glycolate (20) (Reaction XIII).

(Reaction XIII)



In general, the acid catalyzed esterification of organic acids can be accomplished easily with primary or secondary alkyl or aryl alcohols, but tertiary alcohols usually give carbonium ions which lead to dehydration. The structure of the acid is also of importance. As a rule, the more hindered the acid is alpha to the carbonyl carbon the more difficult esterification becomes (20A).

Even more facile than the reaction of an acid with an alcohol is the reaction of an alcohol with an acyl halide (Reaction XIV).

$$\mathrm{R\overset{\overset{O}{\|}}{C}\text{-}X + R'OH \longrightarrow RCOOR' + HX} \qquad \text{(XIV)}$$

The reaction is of very wide scope (21), and many functional groups do not interfere. A base such as pyridine is frequently added to combine with the HX formed. The alcohol may be primary,

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secondary, or tertiary alkyl, or aryl. Enolic esters can also be prepared by this method, although C-acylation can be a side reaction.

When phosgene is the acyl halide, haloformic esters (22) or carbonates may be obtained (Reaction XV).

$$\mathrm{Cl{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl + 2ROH \longrightarrow RO\overset{\overset{\displaystyle O}{\|}}{C}OR + 2HCl} \qquad \text{(XV)}$$

The alcoholysis of anhydrides (Reaction XVI) is similar in scope to the reaction of alcohols with acyl halides. The reaction is catalyzed by general esterification catalysts, but usually they are not needed unless the anhydride is unreactive or the di-ester (such as a phthalate) is the product sought.

$$\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R + R'OH \longrightarrow RCOOR' + RCOOH} \qquad \text{(XVI)}$$

<u>Reactions with Aldehydes and Ketones</u>. Alcohols may combine additively with other carbonyl compounds; such addition compounds are known as hemiacetals or acetals (Reaction XVII).

$$\mathrm{RC(=O)H + R'OH \xrightarrow{H^{\oplus}} RCH(OH)(OR') \xrightarrow{R'OH} R{-}CH(OR')(OR')} \qquad \text{(XVII)}$$

When the reaction is carried out with a ketone the product is known as a ketal. With low molecular weight unbranched aldehydes and ketones the equilibrium lies to the right. If it is desired to make acetals or ketals of higher molecular weight molecules, the removal of water is necessary to drive the equilibrium to the right (23).

Aldehydes and ketones may be converted to ethers by hydrogenation in an acidic alcoholic solution (24) containing platinum oxide (Reaction XVIII).

$$\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R' + R''OH + H_2 \xrightarrow[H^{\oplus}]{PtO_2} R{-}\underset{\underset{\displaystyle OR''}{|}}{CH}{-}R' + H_2O} \qquad \text{(XVIII)}$$

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Addition to Other Unsaturated Molecules. When isocyanates are treated with alcohols, substituted methanes or carbamates are prepared (Reaction XIX).

$$\text{R-N=C=O} + \text{R'OH} \longrightarrow \text{R-NHCOOR'} \qquad \text{(XIX)}$$

The reaction gives good yields and is of wide scope. Cyanic acid (HNCO) gives unsubstituted carbamates. Although the oxygen of the alcohol is certainly attacking the carbon of the isocyanate, hydrogen bonding complicates the details of the mechanism and the kinetic picture (25).

In a very similar fashion, alcohols react with ketenes to give esters (26) (Reaction XX).

$$\gt\text{C=C=O} + \text{R'OH} \longrightarrow \gt\text{CH-COOR'} \qquad \text{(XX)}$$

The addition of HCl to a mixture of an alcohol and a nitrile in the absence of water leads to the hydrochloride salt of the iminoester (27) (Reaction XXI).

$$\text{RC}\equiv\text{N} + \text{R'OH} + \text{HCl} \longrightarrow \text{R-}\underset{\text{OR'}}{\underset{|}{\text{C}}}\text{=NH}_2^{\oplus}\ \text{Cl}^{\ominus} \qquad \text{(XXI)}$$

This reaction is known as the Pinner synthesis. The salt formed may be converted to the free imino ester by treatment with a weak base. It may also be converted to the corresponding ester by an aqueous acid catalyzed hydrolysis. The Pinner reaction is of a general nature and is applicable to aliphatic, aromatic and heterocyclic alcohols.

Alkoxylation. The reaction of alcohols with ethylene oxide gives polymeric products in which many units of the ethoxy group are incorporated (Reaction XXII). The reaction can be controlled

$$\text{ROH} + n\ \underset{\text{O}}{\text{CH}_2\text{-CH}_2} \xrightarrow{\text{OH}^{\ominus}} \text{R(OCH}_2\text{CH}_2\text{)}_n\text{OH} \qquad \text{(XXII)}$$

by varying reaction conditions. Propylene oxide undergoes the same type of reaction although not as fast due to the hindrance of the methyl group.

Finally, although the hydroxyl group of most alcohols can seldom be cleaved by hydrogenation, certain alcohols such as benzyl are susceptible and often readily undergo reduction (28). The most common catalysts are copper chromite and palladium-on-charcoal. Mixtures of $AlCl_3$ and $LiAlH_4$ have also been used for

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this purpose (29). Though the mechanism of alcohol hydrogenolysis is obscure, in some cases nucleophilic substitution has been demonstrated (30).

Displacement of the Hydroxyl Group

Alcohols are among the most easily obtained reagents of organic chemistry. Because of this, the overall conversion of ROH $\longrightarrow$ RX is of great importance where X is typically a halide, hydride, azide, alkyl or an amine.

This section will provide a survey of the importance in syntheses of replacing a hydroxyl group by other functional groups.

Alkyl Halides. The classical method for converting alcohols to alkyl iodides (31) involves heating the alcohol with iodine in the presence of phosphorus (Reaction XXIII). Like other iodi-

$$6ROH + 2P + 3I_2 \longrightarrow 6RI + 2H_3PO_3 \qquad (XXIII)$$

nations using these reagents, the reaction proceeds through an intermediate ester which is decomposed by the in situ generated hydriodic acid.

For the preparation of bromides and chlorides from alcohols, the corresponding acids, HBr and HCl, are the reagents of choice (32). The mechanism (33) for this reaction is believed to involve a protonated intermediate (Reaction XXIV) which is further attacked by the halide.

$$ROH + HX \longrightarrow RO^{\oplus}H_2 \xrightarrow{X^{\ominus}} RX + H_2O \qquad (XXIV)$$

The observed reactivity gradation for this type of reaction is for the acid: HI > HBr > HCl > HF, and for the alcohols tertiary > secondary > primary.

Other halogenating agents include Ph_2PCl_3 (34), PBr_5 (35), AlI_3 (36), and many sulfur containing reagents (37) of which only thionyl bromide and thionyl chloride have attained wide application. The ultimate choice of the halogenating agent to be used will depend on the stereochemistry desired of the final product (38,39).

Amination. Very few reactions of general scope exist for the direct conversion of alcohols to amines. Among one of the oldest is the Bucherer reaction which is used to convert naphthols (40) and phenols (41) to their amine derivative by reaction with aqueous sodium bisulphite and ammonia (Reaction XXV).

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$$ROH + NaHSO_3 \xrightarrow{NH_3} RNH_2 + NaHSO_3 + H_2O \qquad (XXV)$$

The Ritter reaction (42,42A) is a general method for converting alcohols to amines by reaction with a nitrile and a strong acid (Reaction XXVI). In this reaction only tertiary,

$$ROH + R'CN \xrightarrow{H^{\oplus}} RNHCOR' \xrightarrow{H^{\oplus}} RNH_2 + RCO_2H \qquad (XXVI)$$

secondary and benzylic alcohols react as they form the most stable carbenium ions.

Of commercial interest is the direct reaction of alcohols with ammonia at elevated pressures and temperatures in the presence of a dehydrating catalyst such as alumina gel. This process is known as ammonolysis and gives a mixture of primary, secondary and tertiary amines (Reaction XXVII).

$$ROH + NH_3 \longrightarrow RNH_2 + R_2NH + R_3N \qquad (XXVII)$$

Direct displacements of the hydroxyl group by azide are uncommon, but carbonium ions derived from alcohols are attacked by the azide ion to give organic azides (43) (Reaction XXVIII).

$$R_3COH + NaN_3 \xrightarrow{H^{\oplus}} R_3CN_3 + NaCl \qquad (XXVIII)$$

These azides can be further reacted (44) to give an amine as the final product.

Tosylates. Even though the S_N2 reaction cannot be performed on alcohols, the hydroxyl group can be transformed to a good leaving group by its reaction with p-toluenesulfonyl chloride ($p\text{-}CH_3C_6H_4SO_2Cl$). Such a group is then easily displaced by a variety of nucleophiles in essence achieving the substitution of the hydroxyl group (44A). By far this is one of the most useful methods for converting an alcohol to an alkane, an ester, an amine or any other derivative of a nucleophile.

Dehydration of Alcohols

The dehydration of alcohols is an example of a wide range of elimination reactions having the following general form (Reaction XXIX).

$$RCH_2\text{-}CRHOH \longrightarrow RCH{=}CRH + H_2O \qquad (XXIX)$$

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The dehydration of alcohols can take place both in solution (45) and in the gas phase (46). The general rules for this type of elimination have also been recently reviewed (47). For this reason, it will not be attempted in this section to fully explore the area; instead, only a brief review will be given.

In aqueous acidic solutions of either Brønsted or Lewis acids, the dehydration of alcohols leads to the formation of Saytzeff olefins (48). Dehydration occurs most readily if the alcohol is tertiary. For example, the formation of 1,1-diphenylethylene from methyldiphenyl carbinol (Reaction XXX)

$$(C_6H_5)_2\text{-}\underset{}{\overset{OH}{\overset{|}{C}}}\text{-}CH_3 \xrightarrow{H_2SO_4} (C_6H_5)_2C{=}CH_2 + H_2O \qquad \text{(XXX)}$$

occurs very rapidly just by heating the alcohol with dilute sulfuric acid.

Isoprene has been prepared by dehydration of 3-methyl-1-butene-3-ol (Reaction XXXI) and butadiene from the dehydration

$$(CH_3)_2\overset{OH}{\overset{|}{C}}\text{-}CH{=}CH_2 \longrightarrow CH_2{=}\underset{CH_3}{\underset{|}{C}}\text{-}CH{=}CH_2 + H_2O \qquad \text{(XXXI)}$$

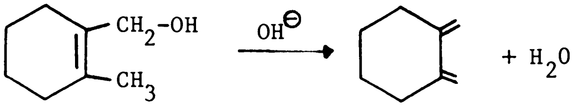
of 1,3-butanediol (Reaction XXXII).

$$CH_3\text{-}\overset{OH}{\overset{|}{C}H}\text{-}CH_2\text{-}CH_2\text{-}OH \longrightarrow CH_2{=}CH\text{-}CH{=}CH_2 + 2H_2O \qquad \text{(XXXII)}$$

The dehydration of 2-pentanol by the sulfuric acid method is of interest since it illustrates the rule that beta-olefins formation is thermodynamically the favored pathway (Reaction XXXIII).

$$CH_3CH_2CH_2\text{-}\overset{OH}{\overset{|}{C}H}\text{-}CH_3 \xrightarrow{H_2SO_4} CH_3CH_2CH{=}CH\text{-}CH_3 + H_2O \qquad \text{(XXXIII)}$$

Alcohols in which the beta-hydrogen is activated by a double bond undergo dehydration by concentrated alkaline media to produce dienes (49) (Reaction XXXIV). Other products such as ethers are possible when the reaction is done in the presence of dimethyl sulfoxide (50).



(XXXIV)

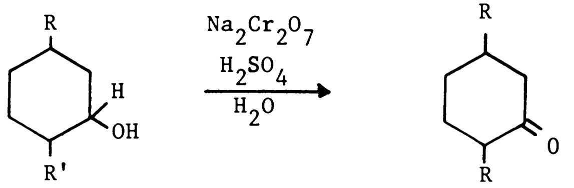
When some straight and branched-chain aliphatic alcohols, such as n-propanol, n-butanol and isopropanol, are subjected to high temperatures, dehydrogenation products predominate over dehydration (51). Presumably the eliminations take place via a six-membered transition state and are catalyzed by hydrogen halides in the homogeneous phase (52) to produce olefins. On the other hand, gas phase dehydration over solid catalysts is a valuable process for the preparation of olefins and ethers.

The most studied dehydration catalysts are the metal oxides (53), but the selectivity of these catalysts in terms of dehydration versus dehydrogenation is not fully understood (54).

Oxidation of Alcohols

Among the many agents available for the oxidation of organic compounds, the ones most commonly used are derivatives of hexavalent chromium (Cr-VI) or heptavalent manganese (Mn-VII). Chromium trioxide (CrO_3) and sodium dichromate ($Na_2Cr_2O_7$) are converted to chromium (III) in the course of oxidations for a total transfer of three electrons to each metal atom. With permanganate in acidic media the manganese (II) ion is formed for a total transfer of five electrons; in neutral or basic media, manganese dioxide is formed with a corresponding transfer of three electrons.

The oxidation of a secondary alcohol to a ketone is usually accomplished with a solution of the alcohol and aqueous acidic chromic acid in either acetone or acetic acid, with a solution of sodium dichromate in acetic acid, or by reaction of the alcohol with aqueous acidic chromic acid as a heterogeneous system. An example is the oxidation of the substituted cyclohexanol below (Reaction XXXV) with sodium dichromate in sulfuric acid (55).



(XXXV)

The course of this dichromate oxidation can be followed spectrophotometrically as the yellow-orange absorption at 350 nm of the chromium VI is converted to green absorption of the chromium III ion (56).

The probable mechanism of oxidation of alcohols by chromium (VI) species involves the formation of chromate esters and their subsequent decomposition to ketones (57). As a rule, in the absence of competing side reactions, the more hindered alcohols react faster than the less hindered compounds. It has also been

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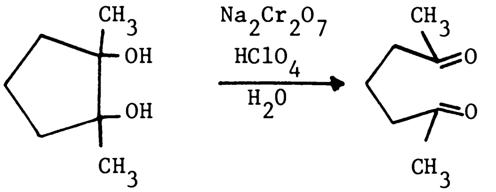
found that electron donating substituents accelerate the rate of oxidation (58).

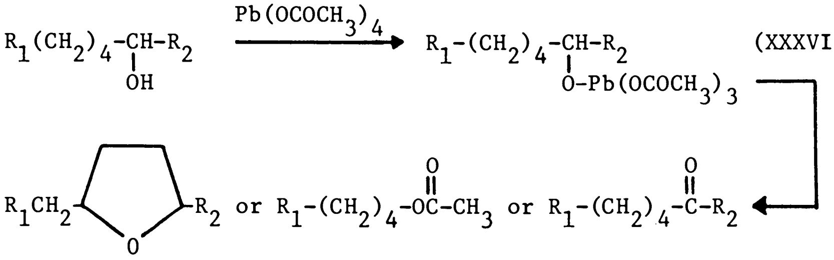
The previously described conditions using dichromate and chromic acid are sufficiently vigorous to slowly oxidize other reactive centers in the molecule such as ethers, amines, carbon-carbon double bonds, and benzylic and allylic C-H bonds. To prevent this, a milder method of oxidation can be used, consisting of adding an aqueous solution of chromic acid (Jones reagent) to an acetone solution of the alcohol to be oxidized (59). Another reagent as mild as Jones reagent consists of a chromium trioxide pyridine complex. This compound can be used for the oxidation of alcohols containing acid sensitive functions such as acetals and ketals (60). A convenient and inexpensive procedure for the oxidation of secondary alcohols to ketones has been reported (60A) to involve reaction of the alcohol with sodium hypochlorite in acetic acid. The yield of the corresponding ketone is around 90 percent with many alcohols. Primary alcohols react slowly giving dimeric ester, presumably via hemiacetal intermediates.

Tertiary alcohols are relatively inert to oxidation by chromic acid; however, tertiary 1,2-diols are rapidly cleaved by chromic acid provided they are capable of forming a cyclic chromate ester (61) (Reaction XXXVI).



(XXXVI)

Monohydric alcohols react rapidly with lead tetraacetate to form alkoxy lead (IV) intermediates. These intermediates decompose thermally or photolytically in a variety of ways to produce ketones, esters, and cyclic ethers (62), as can be seen below (Reaction XXXVII).



(XXXVII)

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Both the structural features of the alcohol and the reaction conditions used are important in determining which of the decomposition pathways is followed. If the lead alkoxide from a primary or secondary alcohol is formed in the presence of a donor solvent, such as pyridine, oxidation to an aldehyde or ketone is the primary mode of decomposition (63) (Reaction XXXVIII).

$$CH_3(CH_2)_3CH_2\text{-}OH \xrightarrow[\substack{\text{Pyridine} \\ 25°C}]{Pb(OCOCH_3)_4} \begin{array}{l} CH_3(CH_2)_3CHO \\ \\ CH_3(CH_2)_3CH_2OCOCH_3 \end{array} \qquad \text{(XXXVIII)}$$

When the oxidations are carried out in the presence of calcium carbonate and lead tetraacetate, the major product is cyclic ethers formed through the intermediacy of free radicals (64).

Analytical Determination of the Hydroxyl Group

Some simple "test tube" reactions can be used to determine the presence and/or the type of hydroxyl groups in organic molecules. Although modern spectroscopy has made the knowledge of this type of analytical chemistry less imperative today, this section will try to cover a few of the most important reactions which are still useful for the fast determination of the hydroxyl group.

(a) Primary and secondary alcohols will react with Nessler reagent (65), a mixture of equal volumes of 2N NaOH and potassium mercury (II) iodide solution. Mix a few drops of the substance with 5 mL of the reagent and boil the mixture for a few minutes. The presence of a primary or secondary alcohol is detected by the formation of a brownish yellow to gray precipitate which turns gray on standing. Tertiary alcohols do not react with Nessler's reagent. A white precipitate may be formed on mixing the reagents, but it dissolves on shaking the test tube.

(b) When added to a solution of n-bromosuccinimide (66), primary alcohols give a stable color, secondary alcohols a fleeting color and tertiary alcohols no color.

(c) Tertiary alcohols are dehydrated when boiled with Deniges' reagent (67); alkenes, which give a yellow precipitate, are formed. The reaction is thus of alkenes, not of tertiary alcohols. Primary alcohols do not react, but some secondary alcohols react almost as readily as the tertiary alcohols.

For a complete treatment of simple qualitative and quantitative reactions for alcohols, the reader is referred to Veibel's book (69) which deals in depth with a large number of analytical reactions.

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Conclusion

In the future, there is no doubt that alcohols will play a major role not only as fuel components (70,71) but also as feed stocks for the syntheses of more complicated organic compounds (72). A great amount of research effort is presently directed to the economic conversion of CO and H_2 to methanol (73), and on homologation of methanol to higher alcohols (74). Conversion of synthesis gas from coal to acetic anhydride (75) through the intermediacy of methyl acetate (from methanol) will soon be a commercial reality.

Dramatic entries have been made into the technology of the eighties by direct utilization of CO and H_2 to produce, for example, methanol and polyhydric compounds (76) (Reaction XXXIX). This unique reaction has attracted considerable attention due to a

$$CO + H_2 \xrightarrow[\text{Bases}]{\text{Rh Catalyst}} CH_3OH + HOCH_2(CHOH)_xCH_2OH \qquad X = 0,1,2 \qquad \text{(XXXIX)}$$

relatively high specificity to ethylene glycol, and to the unusual type of catalysts which bears superficial relationship to homogeneous catalytic systems (77).

Other advances include the commercialization of a process to make oxalic acid (78) (Reaction XL).

$$2\ C_4H_9OH + 2CO + 1/2\ O_2 \xrightarrow[\text{Cat.}]{\text{Pd}} \begin{matrix} COOC_4H_9 \\ | \\ COOC_4H_9 \end{matrix} \xrightarrow{H_2O} \begin{matrix} CO_2H \\ | \\ CO_2H \end{matrix} \qquad \text{(XL)}$$

It is interesting that hydrogenation of the intermediate dibutyl oxalate would produce the glycol and the starting butanol.

This new area of chemistry is still in its infancy when compared to the other reactions covered in this chapter, but many exciting developments can be anticipated in the future.

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2

Methanol: Manufacture and Uses

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This paper covers the current technology of methanol production, reviews how the energy crisis and the escalation of hydrocarbon feedstocks impact that technology, and describes conventional, new, and potential uses for methanol. Methanol is a chemical intermediate and solvent produced from several feedstocks and is consumed in a variety of end uses. Prior to the development of a synthetic route to methanol, commercial quantities were obtained from the destructive distillation of wood or other biomass. Now, with interest focused on conservation and the use of renewable resources, methods have been proposed to use biomass again as a methanol feedstock. While some of these proposals hold great appeal, they are still speculative and beyond the scope of this paper. (Methanol from wood is discussed in the following chapter.)

Methanol Production

Methanol is produced by the catalytic reaction of carbon monoxide and hydrogen (or synthesis gas) in a converter according to the reaction:

$$CO + 2H_2 \longrightarrow CH_3OH$$

Figure 1 depicts a typical methanol synthesis scheme:

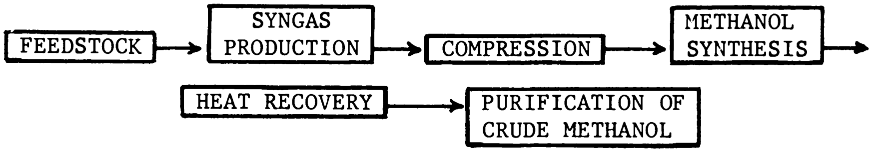

Figure 1. Methanol synthesis summary

Synthesis Gas. There are three principal routes to synthesis gas: steam reforming, partial oxidation, and coal gasifica-

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tion. Steam reforming is limited to lighter hydrocarbon feedstocks, primarily methane and naphtha. Partial oxidation can use not only those light feedstocks, but also heavier feedstocks like residual oil. Coal gasification, applicable to all types of coal, anthracitic to lignitic, is an emerging technology with several competing processes (1).

Thus a variety of hydrocarbons, ranging from natural gas to coal, are used in methanol production. Regardless of the feedstock used to prepare the synthesis gas, it is necessary to remove sulfur so that the converter catalyst is not poisoned. Before natural gas or naphtha is reformed, the feedstock is desulfurized. In the partial oxidation and coal gasification processes, the feedstock is first oxidized and the resulting synthesis gas is desulfurized before entering the converter.

Methanol Synthesis. By whatever means produced, synthesis gas is then compressed for feed to the converter. There are two routes for methanol synthesis, a high pressure process requiring compression to about 340 atmospheres, and a low pressure process requiring compression in the range of 50 to 100 atmospheres (2,2A). Because of the inherent economic advantages of the low pressure technology, high pressure units are in the process of being phased out or converted to low pressure. ICI and Lurgi have the two principal low pressure technologies practiced today for methanol synthesis. They differ primarily in the technique used to remove the heat of reaction and thus control temperatures within the converter. This difference results from converter design.

Converter exit gas containing methanol is cooled by heat exchange with cooling water. The condensed methanol and water mixture is then separated. This crude methanol is purified in a two or three column distillation. The first column separates light ends from methanol. The second column separates methanol from water and fusel oils. If very low ethanol content is required, a third column can be used for final purification.

Impact of Energy Crisis. The two principal steps in methanol production, synthesis gas preparation and methanol synthesis, have been greatly impacted by the continuing energy crisis. Synthesis gas production has been influenced by the relative value of its hydrocarbon feedstocks, and methanol synthesis by the improvements in the energy balances of the newer low pressure technologies. Most synthesis gas production for methanol is based on steam reforming of natural gas. Until recently, many units outside the U.S. utilized naphtha as a feedstock. Steam reforming of naphtha produces a synthesis gas containing hydrogen and carbon in a ratio close to theoretical requirements for methanol synthesis. As the price of crude oil has skyrocketed, the price of naphtha has followed and made naphtha uneconomic versus natural gas as a methanol feed. In the U.S. natural gas has always been the economic choice because of the

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relative abundance of reserves that existed on the Gulf Coast. While the energy crisis has caused a tremendous increase in the price of natural gas, the even more dramatic increase in world oil prices makes natural gas the economic choice for feedstock over naphtha. However, steam reforming of natural gas produces a hydrogen to carbon oxides ratio of about 3:1. To satisfy the stoichiometric requirements for the methanol synthesis reaction, an external source of carbon, usually carbon dioxide, can be added to the feed, and/or excess hydrogen can be purged from unreacted synthesis gas and used as a fuel for the reformer.

Partial oxidation has more recently attracted attention because of its ability to utilize the least valuable portion of the crude oil barrel (3). Partial oxidation of residual oil generates synthesis gas with a hydrogen to carbon oxides ratio of about 1:1. To adjust the synthesis gas to the required composition, a portion of the gas stream is sent to a shift converter where CO and water are converted to hydrogen and CO_2 according to the water gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$

The carbon dioxide is removed before returning the hydrogen to the make up gas stream.

The escalation of oil prices has caused even residual oil prices to rise to a point where coal has attracted interest as a feedstock for synthesis gas in methanol production. Several plants now exist in other parts of the world based on coal gasification. Coal is gasified in the presence of oxygen and steam at high temperatures. Like synthesis gas prepared from residual oil, the hydrogen to carbon oxides ratio is about 1:1 and must be adjusted to a higher ratio utilizing the water gas shift reaction. Table I summarizes the feedstock, process, and hydrogen:carbon oxides ratio of the competing feedstocks.

TABLE I

METHANOL FEEDSTOCKS

	FEEDSTOCK	SYNGAS MANUFACTURE PROCESS	HYDROGEN:CARBON OXIDES RATIO
1.	NATURAL GAS	STEAM REFORMING	3:1
2.	NAPHTHA	STEAM REFORMING	2:1
3.	RESIDUAL FUEL OILS	PARTIAL OXIDATION	1:1
4.	COAL	GASIFICATION	1:1

The energy picture for the future remains cloudy, and the relative costs of competing feedstocks difficult to project with

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any certainty. Increasingly it appears that coal will be the long term economic choice for synthesis gas feedstock. Yet, in those areas of the world where natural gas is in excess supply, gas remains the more attractive feedstock for synthesis gas in methanol production. The capital costs are much lower. The hydrogen:carbon oxides ratio is better for methanol synthesis, and the sulfur removal step is minimized. Oxygen is not required, and the solids handling problem is eliminated. For these reasons, it is likely that methanol plants will be built outside the U.S. in the 1980's in areas of excess natural gas supplies, and methanol from these plants will supply part of U.S. demand.

As previously stated, the high pressure process to convert synthesis gas to methanol is being phased out in favor of the low pressure process because of the latter's inherent economic advantages. These advantages include lower capital costs, lower energy requirements and lower maintenance costs. The first commercial synthesis of methanol had been carried out in a reactor at a pressure of about 340 atmospheres. High pressure processes use a zinc/chromium catalyst that is rugged and poison resistant. However, these catalysts exhibit poor activity, necessitating high temperatures (325°-375° C) and pressures for commercial use (4).

Most existing units are low pressure processes or are being converted to low pressure technology. Reduction in synthesis pressure requires a reduction in temperature. Lower temperatures necessitate a more active catalyst. The activity and selectivity of copper based catalysts for methanol synthesis had been known prior to commercial utilization (2). The stumbling block, preventing earlier use of the catalyst, is the sensitivity of the catalyst to sulfur. This has been solved by the development of methods to remove sulfur from natural gas before it is reformed (4). Since the first low pressure methanol plant was started up in 1966 (2), most new plants have been of that design, and the energy crisis has resulted in the ongoing conversion of the remaining high pressure units to the low pressure process.

Current Applications

Methanol has long been an important item of commerce, resulting from the availability of low cost raw materials coupled with the development and refinement of an efficient synthetic process. Despite having been directly and greatly impacted by the ongoing energy crisis, methanol remains a relatively inexpensive solvent and chemical intermediate with a myriad of uses. While many of these uses are mature with only minimal growth forecast, newer end uses continue to be commercialized, spurred by economic factors, namely availability and low cost. Today, over three billion gallons of methanol are produced and consumed in the world annually with the U.S. accounting for nearly one

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third of the total. Growth is forecast to approximate twice the rate of growth in GNP (5).

Conventional uses of methanol account for 90% of present consumption and include formaldehyde, dimethyl terephthalate, methyl methacrylate, methyl halides, methylamines and various solvent and other applications. Newer uses for methanol that have revitalized its growth and outlook include a new technology for acetic acid, single cell protein, methyl tertiary butyl ether-(MTBE), and water denitrification. Potential uses for methanol include its use as a carrier for coal in pipelines, as a source of hydrogen or synthesis gas used in direct reduction of iron ore, as a direct additive to or a feedstock for gasoline, peak power shaving and other fuel related possibilities. Table II lists the world methanol demand by end use in 1979.

The largest and oldest chemical intermediate use for methanol is formaldehyde. Over half of the methanol currently consumed in the world goes into formaldehyde production. Formaldehyde is produced by the catalytic oxidation or the oxidative dehydrogenation of methanol. The major outlet for formaldehyde is amino and phenolic resins. These resins are in turn used in the manufacture of adhesives for wood products, molding compounds, binders for thermal insulation and foundry resins. Formaldehyde is also consumed in the production of acetal resins, pentaerythritol, neopentyl glycol, trimethylolpropane, methylenediphenyldiisocyanate (MDI), and textile treating resins.

Dimethyl terephthalate (DMT) is produced either by the esterification of terephthalic acid or the esterification of monomethyl terephthalate produced by oxidation of methyl p-toluate. DMT is consumed in the production of polyethylene terephthalate, the polymer used in the manufacture of polyester fibers, films and bottle resins. Terephthalic acid (TPA) is also used in the production of polyethylene terephthalate but does not consume methanol. Since TPA is continuing to increase its share of the market, DMT is expected to exhibit slower growth than the overall market for polyethylene terephthalate.

Methyl methacrylate, accounting for 4% of methanol consumption, is produced by the cyanohydrin process utilizing methanol. Methyl methacrylate is used to produce acrylic sheet, surface coating resin, and molding and extrusion powder. Also, there exist minor miscellaneous uses such as modification of acrylic fiber and polyester resin.

Methanol consumed in the production of methyl halides and methylamines accounts for 8% of consumption. Methyl chloride is made by the reaction of hydrochloric acid and methanol. Methylene chloride and chloroform are produced by chlorinating methyl chloride. Methylamines are produced by catalytically reacting ammonia with methanol. Methyl chloride is used in the production of silicones and tetramethyl lead. Methylene

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TABLE II

WORLD METHANOL DEMAND

1979

END USE	PERCENT OF TOTAL METHANOL CONSUMPTION
Formaldehyde	52
Dimethyl Terephthalate	4
Methyl Methacrylate	4
Methyl Halides and Methyl Amines	8
Acetic Acid	6
MTBE	4
Single Cell Protein	<1
Solvents	8
Miscellaneous	14
	100%

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chloride is used as a solvent, urethane blowing agent and aerosol propellant. Chloroform's principal uses are in the manufacture of propellants and in the production of flurocarbon plastics. Monomethylamine is consumed in the production of insecticides and surfactants. Dimethylamine is used in the production of spinning solvents for acrylic fibers, surfactants, insecticides and rubber chemicals.

Solvents account for 8% of methanol demand and include process uses such as extracting, washing, drying and crystallizing. Miscellaneous uses of methanol include the production of glycol methyl ethers, methyl acrylate and methyl acetate. Other uses include antifreeze, gasoline deicer, windshield washer fluid and hydrate inhibition in natural gas.

New Applications

As seen from the above, conventional uses of methanol cover a wide range of products which in turn find application in a very broad cross-section of industrial and consumer goods. New end uses have continued to develop and spur the growth of methanol production. One such development is the Monsanto low pressure process that carbonylates methanol to acetic acid (6). Essentially all new acetic acid capacity now being installed is based on Monsanto technology. By 1981, eleven plants converting methanol to acetic acid are scheduled to be on stream. At capacity they will consume over 300 million gallons of methanol.

Another emerging use of methanol is methyl tertiary butyl ether (MTBE), a compound which improves the octane rating of gasoline (7). It is produced by the selective reaction of methanol with isobutylene over ion exchange resin catalyst. Government regulations requiring unleaded gasoline and improved mileage provide impetus for the development of an octane improver which does not add lead to the atmosphere or affect automobile hydrocarbon emissions. MTBE, while not a replacement for tetraethyl lead or MMT (methylcyclopentadienyl manganese tricarbonyl), is a relatively high octane blending stock for gasoline. MTBE has been produced in Europe since 1973. There is capacity in Europe to produce 220 thousand tons of MTBE which requires about 27 million gallons of methanol. In the U.S., the EPA gave approval in early 1979 for the addition of MTBE to unleaded gasoline. Since then several units have been brought on stream in the U.S. Present U.S. MTBE capacity is 380 thousand tons which requires about 48 million gallons of methanol. When all the announced plants are brought on stream and run at capacity, 180 million gallons of methanol will be required for MTBE worldwide.

Methanol appears to be the preferred carbon source for single cell protein production though several hydrocarbons could be used. Bacteria is grown in a mixture of air and methanol containing ammonia, water and other mineral nutrients. An ICI

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plant that recently was brought on stream has the capacity to produce 75 thousand metric tons of SCP for primary use as an animal feed additive (8). When run at capacity, the plant will consume 50 million gallons of methanol. An optimistic potential for methanol consumption in SCP production would be in the several hundred million gallons range by the mid-1980's. Whether this projection is realized or not depends on 1) the ability of single cell protein to compete with soybean as a protein source, 2) successful handling of regulatory, environmental and agricultural opposition and 3) methanol not being displaced by a cheaper carbon source.

Very small quantities of methanol are now consumed in the denitrification of waste water. Methanol is used as a carbon source by bacteria which convert nitrates and nitrites to nitrogen. Methanol is an efficient carbon source and decreases the production of byproducts. The potential requirement for a carbon source for water denitrification is large but the use of methanol is threatened by cheaper feedstocks. One large denitrification plant in the U.S., for example, uses brewery waste as a carbon source. In the future, water treatment plants designed for water denitrification may utilize a less expensive alternate carbon source than methanol.

Fuel uses are a potential application which would require substantial volumes of methanol. As mentioned earlier they are reviewed in the following chapter. A fuel related potential use of methanol is as a replacement for water used to carry coal in pipelines. Methanol is being considered for this use because it would eliminate a demand for water, which is often scarce in areas where coal is mined, and methanol could be burned as a fuel with the coal at its destination. Methanol has also been touted as a good feedstock for gases used in the direct reduction of iron ore. If this use of methanol is realized, it will not be before the mid to late 1980's. Other potential new uses for methanol include a feedstock for ethylene and propylene production (9) and a feedstock for gasoline production (10).

Conclusions

In conclusion, this review traces the evolution of methanol technology as well as its applications. This dynamic industry is being challenged by the energy crisis. In response to this challenge, the industry is developing efficient, flexible, evolving technologies and looks forward to a future of continued growth.

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3

Methanol from Wood in Brazil

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The Brazilian economy has been severely damaged by continuous increases in crude oil prices. Domestic production of fossil fuels is small, and this year oil imports will demand 40% of all export revenues. There has been a chronic deficit in the balance of payments and monies spent are not recycled within the country. Also, other countries that traditionally import Brazilian goods tend to adopt protectionist trade policies to balance their own external trade.

The primary energy consumption in Brazil is as shown in Table I (1):

Table I
Primary Energy Consumption in Brazil (1977)

Source	Daily consumption (1 000 Bbl)	(%)
Imported oil	720.3	34.9
Brazilian oil	141.0	6.8
Imported coal	54.0	2.6
Brazilian coal	28.1	1.4
Hydroelectricity	539.1	26.1
Wood	417.7	20.2
Others (natural gas, ethanol, charcoal, bagasse)	164.8	8.0
TOTAL	2,065.0	100.0

Imported oil in the Brazilian energy matrix does not appear large when compared with most of the OECD countries. The major problem is that Brazil has great difficulty increasing exports to compensate for the continuing rise in oil prices. Brazil is practically compelled to reduce its imports. The gross national product must increase at least 6% per year to avoid social problems that would come with unemployment. The energy demand increase associated with this growth is around 5% (historically this rate has been around 10% annually over the past 20 years). Annual energy consumption per capita is around 900 kg of oil

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equivalent (20th place in the world ranking) which indicates that conservation policies will lead to small but not negligible effects. On the other hand, oil prices are expected to rise until they reach the cost of producing the cheapest large scale synthetic fuel. Under such conditions it is reasonable for Brazil to produce synthetic fuels, even with costs higher than the present oil price.

The energy blend in Brazil is not very dependent on imported oil (85% of 42% = 35.7 in 1978) (2). Therefore, the partial substitution of a more expensive domestically produced synthetic fuel for imported oil would have little impact on average energy costs for the country. As oil prices tend to rise, possibly up to the level of synthetic fuels costs, the risk of having too expensive energy is very small in Brazil. On the contrary, Brazil may obtain quite an attractive situation with regard to energy supplies.

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Biomass Energy in Brazil

Brazil is a very large country with a warm and rather humid climate, which permits large, economical production of biomass. Nowadays, wood and charcoal are responsible for 25.7% of the total energy supply in the country. So, the intensive utilization of energy from biomass does not represent something really new. In the forties more than 50% of its energy was obtained from biomass (mainly wood). In order to produce liquid fuels from biomass, basically two routes can be adopted:

- production of ethanol through fermentation;
- production of gas, followed by synthesis of fuels (methanol for example).

Potential production rates of energy (expressed in Mcal/ hectare/year) in the form of alcohol, through biomasses that are already extensively planted in Brazil, are shown in Table II (3):

Table II
Potential Production Rates of Energy in Brazil

Crops	Fraction of Occupied Land	Energy (alcohol)	Agricultural Production Energy	Net Liquid Energy
Sugar cane	100 %	18,020	3,796	14,224
Cassava	81 %	10,332	2,431	7,091
Eucalyptus (ethanol)	87 %	12,373	551	11,822
Eucalyptus (methanol)	73 %	18,407	551	17,856
Pinus (ethanol)	85 %	16,464	471	15,993
Pinus (methanol)	68 %	21,362	471	20,891

Fraction of occupied land represents the fraction of the total area occupied by crops; the remaining part is occupied by Eucalyptus culture, for supplying energy to the plant, if necessary. The following raw material production per hectare per year is assumed:

- eucalyptus: 11.8 tons (oven dried material)
- pinus: 14.6 tons (oven dried material)
- sugar cane: 55 tons

Brazil has produced ethanol as a fuel since 1930. Table II shows that productivity of methanol from wood is better than ethanol from sugar cane and much better than ethanol from wood. This fact plus the convenience of not being dependent on just one crop and the possibility of using poor lands for reforesting indicated that the production of methanol from wood should be more deeply evaluated.

The Methanol Option

Brazil made an option for alcohol fuels in 1975, when it started the PNA - Programa Nacional do Álcool - that led to the production of nearly four million cubic meters of ethanol in 1979, equivalent to 20% of the total gasoline consumption. The necessary investment was small, as the international market for sugar had undergone a very severe crisis, with very low prices and little demand, between 1974 and 1978. Investments made in sugar cane production and sugar mills, that would otherwise remain useless, have been utilized to produce ethanol for marginal costs. The whole agricultural, industrial and managerial infrastructure was available, and so ethanol production grew at a 35% yearly rate between 1970 and 1978. It is expected to grow at 17% yearly for the next eight years, reaching ten million cubic meters in 1986.

Even considering the very unique conditions that Brazil has to produce ethanol, its cost is quite high (around US$ 1.10/ gallon). Furthermore, as said before, it is not desirable for Brazil to remain so dependent on sugar cane. Methanol from wood appears to be the natural complement to the existing ethanol industry and market. The cost of methanol production seems very attractive. Its large scale production does not present any serious technological problem. Only the gasification system to process large amounts of wood has to be developed, but this is not a difficult problem. Brazil has considerable experience in reforestation, for cellulose and charcoal production. More than three million hectares are already planted and 300,000 hectares are being planted yearly. Increasing this rate of reforesting is not a major problem. The most important point is to prove the economic feasibility of methanol production in Brazil.

Production Routes

Figures 1 and 2 show the process routes for methanol synthesis. The first one is based on a fluidized bed and includes a pressurized gasifier (Winkler type) that produces a very clean gas, practically free of tars and other impurities from wood distillation. The second route is based on a fixed bed

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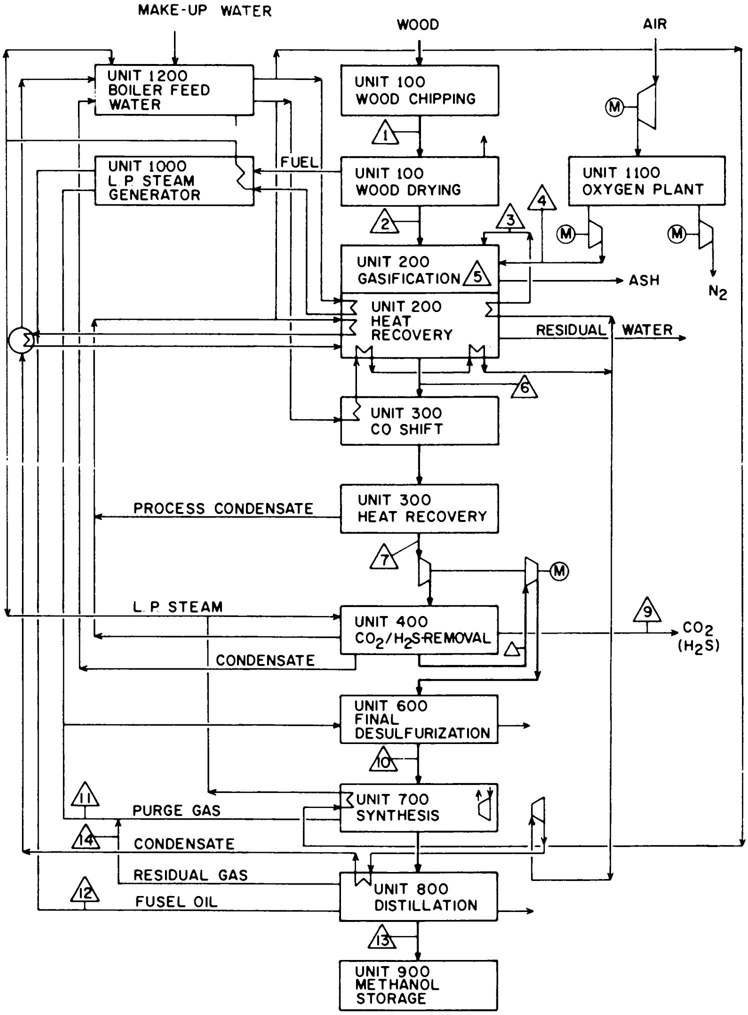

Figure 1. Methanol synthesis—Winkler gasifier

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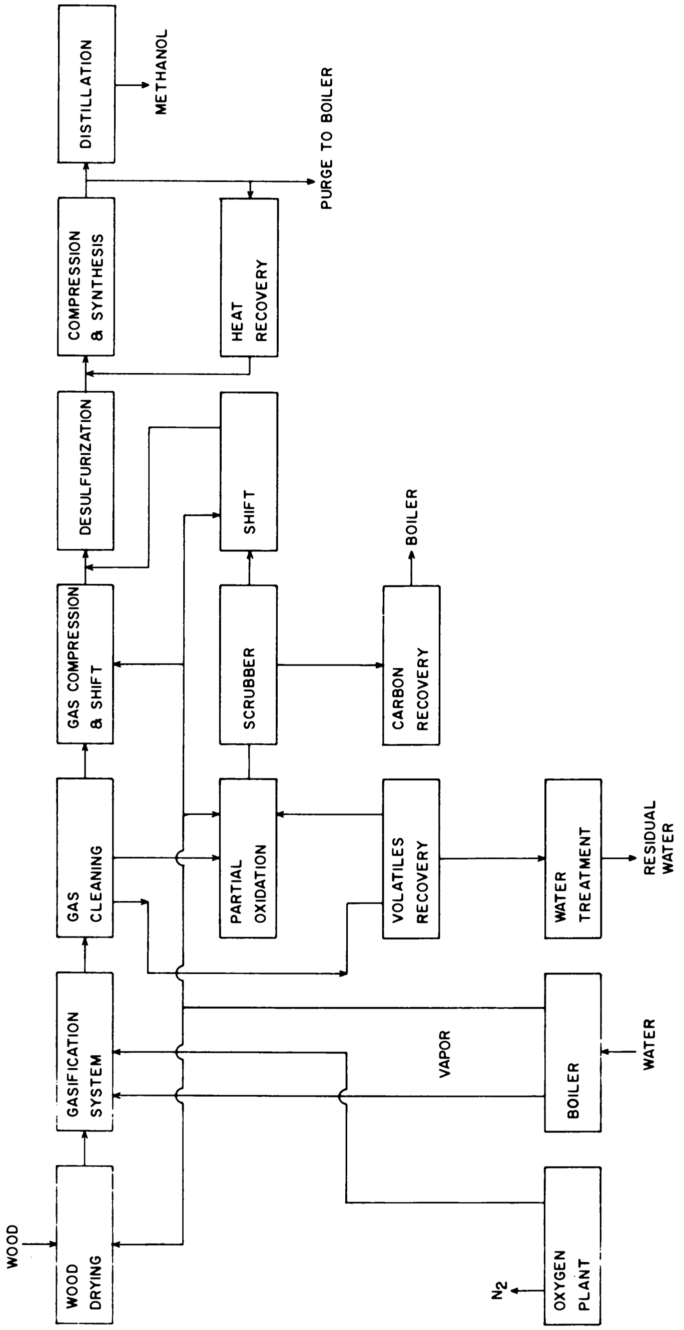

Figure 2. Methanol synthesis—conventional gasifier

In Monohydric Alcohols; Wickson, E.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1981.

conventional gasifier that produces a gas containing large amounts of tars that have to be washed out. The tars can be used for steam generation or, depending on the thermal balance of the plant, can be sent to a partial oxidation unit. All the plant sections are conventional, except the gasification system.

Material and Energy Balance

A 1,000 ton/day methanol plant, using a Winkler type gasifier adapted to burn wood chips and to use the ICI process for synthesis, requires the following consumption of ingredients per ton of methanol:

- wood (30% moisture) = 2.6 t
- electricity = 720 kWh
- cooling water = 115 m^3
- clean water = 1.5 m^3

If ones utilizes conventional gasifiers operating at atmospheric pressure, such as the Davy or Lacotte type, raw material consumption goes up. This also applies if charcoal is used as a raw material. The main reasons are that much of the tars is lost and more energy is needed to compress the gases.

	Conventional wood gasifier	Charcoal gasifier
Wood (30% moisture)	3.1 t	~ 4 t
Charcoal	-	1.1 t
Electricity	1,250 kWh	790 kWh
Cooling water	115 m^3	135 m^3
Clean water	1.5 m^3	1.6 m^3

Adopting 4,770 kcal/kg for the low heat value of methanol and considering the case of a Winkler type gasifier, the energy balance of the plant would be as shown in Table III:

Table III
Energy Balance of Methanol from Wood Plant

Item	Input Gcal/hour	Output Gcal/hour
Wood (30% moisture)	331.1	-
Water	0.7	-
Electricity	25.6	-
Compressed air	7.0	-
Methanol	-	198.8
Losses		
Residual air	-	23.7
Combustion gases	-	3.3
Cooling water system	-	45.0
Gas cooling system	-	75.5
Others	-	18.1
TOTAL	364.4	364.4

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The net overall efficiency is around 55%, less than the figure for methanol plants using natural gas with efficiencies as high as 65%.

Fixed Investments and Raw Material Costs

Investments. Several studies have been published, evaluating the investment costs of methanol production from coal, lignite and biomass. The set of values have been selected as shown in Table IV:

Table IV
Investment Costs of Methanol Plants

Reference	Raw Material	Capacity t/day	Total Investment Cost (US$ x 10^6)
(4)	wood	1,000	137
(8)	wood	500	64
(8)	wood	2,000	169
(7)	coal	2,000	330
(6)	coal	2,500	306
(6)	coal	1,000	150
(9)	coal	5,000	531
(9)	coal	1,000	141
(9)	lignite	5,000	630
(9)	lignite	1,000	178

From these numbers we may deduce that:
- Investment costs in methanol plants from wood, coal or lignite have the same order of magnitude. For a 1,000 t/day plant this cost is in the range US$ 140 to 180 million under present conditions in Brazil.
- Investment costs for methanol plants from wood ought to be less than for methanol plants from coal because wood has a very low ash content and is practically free of sulfur.
- Methanol production is not a "capital intensive" process as compared to other synfuel production systems. Fixed capital cost is between US$ 0.21 and 0.35 per liter/year of installed capacity. This investment cost is similar to that needed for ethanol production in Brazil.

The cost breakdown (4) is as shown in Table V:

Table V
Investment Cost Breakdown

Item	% of total cost
Process equipment	30.3
Auxiliary equipment	8.8
Off sites	2.2
Civil work	3.6
Erection	18.7
Engineering and administration	9.8

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Licensing	1.5
Spare parts	3.0
Transportation and insurance	9.1
Interest during construction	13.0
	100.0

For a plant in Brazil it is important to verify that the amount to be paid in foreign currency is about 30% of process equipment and engineering, plus licensing costs. Total imports will represent about 13% to 15% of the total investment costs.

Wood Costs and Productivity. The F.O.B. costs for wood in the States of São Paulo and Mato Grosso do Sul are as follows:

	Costs ($US\$/m^3$)	
Item	São Paulo	Mato Grosso
Standing wood	4.00	1.96
Exploration	2.24	2.24
Transport	5.60 (100 km)	7.28 (200 km)
TOTAL	13.60	11.48

Wood transportation represents almost 50% of its F.O.B. cost. Thus it is a very important item to be considered in site selection. Assuming for wood a heat value around 3,500 kcal/kg (30% moisture) the energy cost will be between US\$ 4.68 and 5.55/Gcal or US\$ 1.2 and 1.4 per million BTU.

The wood costs above are very close to the price paid to wood producers by the cellulose plants in the State of São Paulo.

The wood cost per ton of methanol produced is between US\$ 42.8 and 64.2 (2.6 to 3.0 t of wood per ton of methanol). These costs can be reduced if the plant is located inside the forest itself.

The average value of wood productivity (in m^3/ha per year) is a function of the soil characteristics, seed genetics, micro-climate, cycle of cutting, and other parameters. For the average Brazilian situation, eucalyptus industrial forests, planted in poor lands (cerrado, a type of savanna, for example) and cut every 7 years, have a production of 20 t/ha per year (50% moisture) which permits production of 5 to 7.7 tons of methanol/ha per year.

Operating Costs.

a) Manpower: the required manpower can be defined as follows for a plant with production capacity of 1,000 tons of methanol/day:

- engineers - 12
- technicians - 193
- labor - 295

TOTAL 500

In Monohydric Alcohols; Wickson, E.;
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The expenditure for the above mentioned group, including social benefits, can be estimated at US$ 5.57 million per year. The man-hour cost participation in the total production cost is of the order of US$ 18.6 per ton.

b) Electricity: if the synthesis compressor and the oxygen plant section are electrically driven, the total electrical power requirement for the plant is 29.7 MWh/h for 1,000 t/day methanol production. If no cheap electricity is available, it is possible to use steam driven compressors. In this case wood consumption is increased 15% and electric power is reduced to 7.1 MWh/h.

The above analysis assumes cost of electricity is US$ 30/MWh, which is the average industrial electricity rate in Brazil.

c) Catalysts and chemicals: one may adopt US$ 1.5/t of methanol, on the basis of international and Brazilian experiences.

d) Maintenance: for the type of plant considered, it is reasonable to estimate maintenance costs as 2.5% of the total investment, amounting to US$ 3.425 million per year.

Production Costs

From the preceding values, the following production costs (US$/t of methanol) are shown in Table VI:

Table VI
Methanol Production Costs

Item	Wood Gasifier	Conventional Gasifier	Conventional Charcoal Gasifier
Raw material (wood or charcoal)	41.8	49.8	64.2
Electric power	21.6	37.5	23.7
Labor	18.6	18.6	18.6
Catalysts	1.5	1.5	1.5
Maintenance	11.4	11.4	11.4
TOTAL	94.9	118.8	119.4

Capital costs should be added to these costs, calculated for an amortization period of 20 years, 10% yearly interest, annual production of 300,000 t of methanol (plant service factor = 82%), as indicated below:

Investment Level (US$ x 10^6)	Capital Costs (US$/t of methanol)
100	39
120	47
140	55
160	63
180	70
200	78

Consequently, total production costs (as a function of the

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investment level and of the adopted technology) are shown in Table VII:

Table VII
Total Production Costs of Methanol

Investment	Gasification Process		
	Winkler	Conventional (wood)	Conventional (charcoal)
US$ x 10^6	US$/t	US$/t	US$/t
100	132	158	158
120	142	166	166
140	150	174	174
160	158	182	182
180	165	190	190
200	173	198	198

As the required investment is between US$ 140 and 180 million the cost of methanol from wood is between US$ 150 and 165/t using advanced technology, and between US$ 174 and 190/t using traditional gasification systems.

Methanol Costs and Oil Prices

There is no accurate way to determine the real costs of the various oil derivatives. Oil refining is a continuous operation and it is very difficult to allocate costs to each derivative obtained. In Brazil this question involves certain social criteria, aimed at reducing or increasing the consumption of a given derivative, minimizing social effects of oil price increases, fostering the development of some branches of industry, etc. It is certain that the average price attributed to the various derivatives should cover all refining costs, including the capital costs of the refineries.

To compare costs of methanol and oil derivatives, it is advisable to take the real costs of methanol and the average refining costs of the various derivatives, while also considering the corresponding heat contents and efficiencies in each use. In an economical macroanalysis there is no sense in comparisons based just on market prices.

In a very simple way, it can be stated that the production cost of methanol should be kept below an upper limit (or maximum acceptable cost) given by the expression:

$$Cm = \frac{Cp + Cr}{159} \times \frac{H.V.m.}{H.V.oil} \times \eta$$

Cm = maximum acceptable production cost of methanol (US$/liter)
Cp = F.O.B. price of oil (US$/Bbl)
Cr = refining and transportation cost of oil (US$/Bbl)
H.V. methanol/H.V. oil = heat value relationship
η = efficiency in the substitution of methanol for a given

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oil derivative.

The following data might be considered:

Cp = varying from US$ 25 to US$ 50/Bbl

Cr = US$ 6/Bbl (average Brazilian costs) (10)

H.V. methanol = 4,700 kcal/kg

H.V. oil = 10,500 kcal/kg

η = depends on the derivative to be substituted.

- Partial substitution for gasoline: utilizing up to 15% methanol, compression ratios of the engines in Brazil could be increased. The fuel consumption does not follow the proportion based on the heat values. Practically the η value is around 1.4, similar to ethanol.

- Complete substitution for gasoline: in this case the gain in efficiency is not very high. The experience with ethanol indicates $\eta \simeq 1.2$.

- Diesel oil substitution: tests made by CESP/IMT (5) indicate that for producing 1 kWh net with diesel engines requires 11.5 MJ of diesel oil or around 10.5 MJ of methanol, which indicates $\eta \simeq 1.1$.

- Fuel oil substitution: $\eta \simeq 0.90$.

The values of Cm (methanol) are shown in Table VIII, in US$/t, for oil prices varying from US$ 25 to 50/Bbl, and various types of oil substitution:

Table VIII

Maximum Acceptable Methanol Production Costs

Substitution \ Oil price US$/t	25	30	35	40	45	50
Partial substitution	153	177	202	227	252	276
Complete substitution	131	152	173	195	216	237
Diesel oil substitution	120	139	158	178	198	218
Fuel oil substitution	98	114	130	146	162	178

At present oil prices, around US$ 30/Bbl, the Cm values are between US$ 114 and 177. As oil prices tend to rise and methanol costs remain practically fixed, methanol as a fuel becomes an economically feasible alternative under Brazilian conditions and its feasibility tends to improve as oil becomes more and more expensive and difficult to obtain.

CESP's Experiments in the Production of Methanol from Wood

CESP - Companhia Energética de São Paulo - has developed tests on charcoal and wood gasification, as well as methanol synthesis, in a pilot plant (Corumbataí) in Rio Claro, State of São Paulo. The plant produces 20 kg/hour of methanol using two charcoal gasifiers and has been designed to produce 1,000 kg/day of methanol directly from wood with a third gasifier that has been operating since September, 1980.

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The main objectives of the plant are:

- to define operational, technical and reliability aspects of charcoal and wood gasification
- to develop alternative technologies for wood and charcoal gasification and synthesis gas treatment
- to promote alternative catalyst tests, defining their main characteristics
- to evaluate Brazilian capability in equipment manufacture and design, engineering and erection of gasification systems, high pressure plants, methanol synthesis, utilities, etc
- to aid in training operators.

Corumbataí Pilot Plant. The flowsheet in Figure 3 shows the main process diagram and its equipment.

A - Low pressure area

. Gasifiers: two units using charcoal
  one unit using wood directly
. Gas coolers: three units
. Gas washers: one unit
. Dewatering: one unit

B - High pressure area

. Main compressor: three stages, 55 atm, 64 Nm^3/h capacity
. Shift converter: made of stainless steel, operates at 500°C, iron oxide catalyst
. Desulfurization unit: a stainless steel column, ZnO catalyst, 400°C
. Methanol converter: two stainless steel columns, in series, operating at 300°C and 50 atm, Cu catalyst
. CO2 removal unit: made of carbon steel, operates with 5°C water in spray
. Electric gas heater

C - Services

. Electrical switchyard, 1,200 kVA
. Electric boiler, for superheated steam
. Water cooling unit (for the CO_2 removal unit)
. Methanol storage tanks.

Process description. In both charcoal and wood gasifiers, the carbon monoxide and hydrogen are obtained by passing steam into a bed of charcoal (electrically heated). In the wood gasifier, wood is converted into charcoal by recirculating the hot gases and the wood volatiles from the top to the bottom of the vessel. The hot gases carbonize the wood, and the tars are destroyed by circulating in the hot area of the gasifier (gasification area in the bottom which has a temperature around 1,250°C) thereby generating more synthesis gas.

The final gas temperature is 85°C; it is further cooled to 50°C by direct contact with a water spray, and then washed; the gas passes through a dewatering column and is compressed to 50 atm. Its composition at this stage is:

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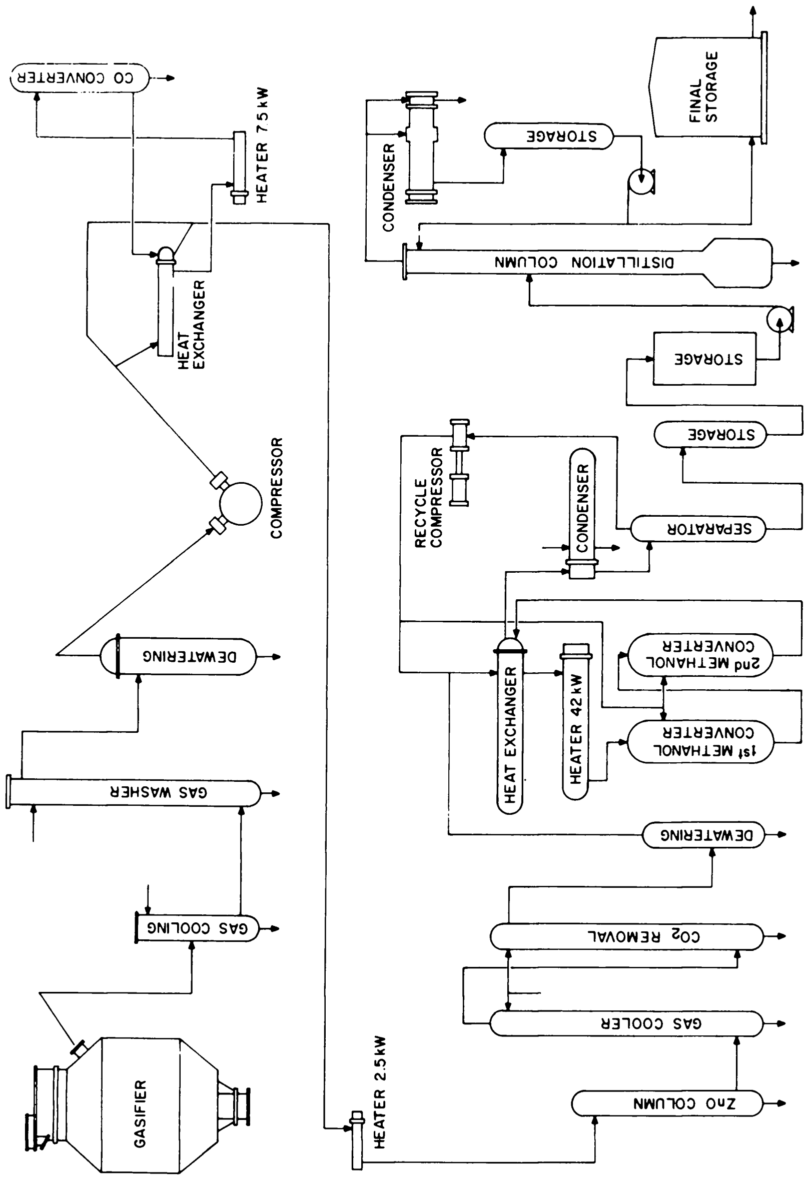

Figure 3. Methanol synthesis—CESP's pilot plant

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H_2 - 50%
CO - 39%
CO_2 - 5%
N_2 - 5%

The synthesis gas composition, as required for the installation, is:

H_2 - 67.4%
CO - 18.8%
CO_2 - 9.4%
N_2 - 4.4%

To achieve this composition, part of the gas flows to the shift converter and, reacting there with the superheated steam, produces CO and CO_2. There is a heat exchanger to raise the temperature of the compressed gas to the shift temperature; the heat comes from the shift reaction. The gas is introduced in a ZnO column, to eliminate sulfur traces, then is cooled with water, and passes through the CO_2 removal column. The CO_2 is absorbed by 5°C water at 50 atm, and the gas is now ready for synthesis.

Before entering the synthesis vessel, the gas is mixed with the recycled gas which is then heated by exchange with synthesis reaction heat; the gas enters the first reactor at 240°C and leaves the second at 270°C. In this exchanger the exit gas exchanges heat with the gas that enters the synthesis reactor; and afterwards it is cooled to 35°C, which condenses the methanol vapors. The liquid methanol is separated and the non condensed gas is recycled.

Just for start up, there are electric gas heaters before the shift, the desulfurization and the synthesis units; during normal operation, these heaters are not used.

Future developments. As mentioned earlier, the major technical problem for the production of methanol from wood is wood gasification. No wood gasifier for large scale gas production is now available, because no one has really been interested in this question for economic reasons. Technically, wood gasification is easy: wood is a very homogeneous material, has low ash and sulfur content, and behaves as a very good fuel. There are various wood gasifiers that operate pretty well for small amounts of wood. Historically, wood and charcoal have been gasified for many decades, mainly in France and also in Brazil, during the Second World War. What has to be done now is to design, build and test some demonstration gasification plants on a commercial scale, in order to define the main design data. Two alternatives lines might be followed:

- to design a completely new wood gasifier
- to adapt some existing coal gasifier to operate with wood.

With a view of saving time, CESP decided on both alternatives.

After an in-depth survey of the available technologies, three options have been made:

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1. To develop and build a wood gasifier using experience from the present pilot plant. This will be a fixed bed unit, with recirculation of wood volatiles; the reaction heat will be obtained partly from electric power and partly through oxygen injection which permits good reaction control and avoids excessive consumption of electricity.
2. To develop and build a wood gasifier and a gas cleaning system using a very traditional technology. This is a very conservative and prudent approach that certainly will give good results. Such a gasifier (fixed bed, atmospheric pressure, counter-current) will actually be the result of updating some units built in India for an ammonia plant just after the Second World War.
3. To adapt for wood an advanced lignite gasifier that operates co-current at 10 atm in a fluidized bed. This system has many advantages, produces a very clean gas, but is now in a very preliminary development stage.

Each of these envisaged units will produce an amount of gas equivalent to 100 t of methanol per day, burning around 300 t of wood per day. The engineering development for the three units is just beginning and is being carried on by joint ventures of Brazilian, American and German private companies, one for each unit. All units are scheduled to operate by the end of 1981.

CESP's Experience in Using Methanol as a Fuel

Methanol can be used as an alternative fuel for gasoline, diesel and fuel oil. Tests are being made for these three alternative uses. The methanol fuel will substitute for oil derivatives defined by Brazil's energy policy. What has to be done now is to verify the technical advantages and disadvantages to each form of utilization.

Gasoline substitution. Two General Motors vehicles are operating in their normal work, using methanol as a fuel. One has a 6 cylinder engine, the other a 4 cylinder engine. Modifications were:

- pre-heating of the air-methanol mix
- more powerful ignitions
- increase in the compression ratio (from 7.5:1 to 11:1)
- substitution for the original carburetor

These vehicles have already run 35,000 km without any problems at all. The 4 cylinder car fuel consumption is 7.3 km/liter and the 6 cylinder (a G.M. pick-up) is 3.7 km/liter.

Other engines, mainly Volkswagen, are being tested in dynamometers to measure the emissions (pollution control) and other general performance data.

For gasoline substitution major problems are not expected. Brazil has used ethanol blended with gasoline for years without problems and now ethanol engines are part of the normal production of the Brazilian car industry. Methanol is very

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similar to ethanol as a fuel. However, by 1985 Brazil is expected to produce ethanol equivalent to 60% of its gasoline demand. Under these conditions, methanol will probably substitute for diesel and fuel oil, the derivatives that are now increasing Brazil's oil importation.

Fuel oil substitution. A 15 MWe thermogenerator has been remodeled to burn methanol. This type of boiler is currently manufactured in Brazil and is widely used here. Its main characteristics are:

Type	VU 60
Capacity of superheated steam	68,000 kg/hour
Steam temperature	440°C
Steam pressure	42.2 kgf/cm^2
Fuel oil consumption	6.4 t/hour
Number of burners	6 (A-20 type)
Efficiency	85%

The main modifications took place in the burners. The boiler itself has not been modified. In the tests it achieved 60% of nominal output of steam. With better monitoring of superheater temperatures, it is expected to achieve an output of 90%. The test program will be developed this year (1980) and will include emission analysis, boiler efficiency, corrosion, and other aspects. CESP also plans to analyse smaller boilers which will operate this same year.

Diesel substitution. Diesel fuel is the basic fuel for the Brazilian transportation system, and structural modifications to this system are very difficult to implement. To substitute for this fuel, several experiments are being carried on by CESP:
- use of additives: research on existing and new additives. Minimum changes are required to adapt the engine. Several vehicles and engines are being used for the tests.
- dual fuel engines: a diesel-electric locomotive operates with methanol and diesel oil. This process is suitable for heavy vehicles requiring two fuel tanks. Consumption of diesel oil is reduced by 50% in preliminary tests at nominal output.
- high compression ratio engines: a four cylinder Detroit Allison engine with a compression ratio of 24:1 was installed in a truck and is operating in normal service, using 85% methanol and 15% castor oil. This engine has operated eight months without any serious problem.
- hot spot: very good results are being achieved by inserting a hot spot (electrical resistance) in the combustion chamber of the diesel engine. Methanol with only 1% castor oil (for injection pump lubrication purpose) has shown good performance, even on cold start.

All of these experiments are in preliminary stages of development. The results obtained until now are very good, but detailed information on fuel consumption, life of the engine, economics, average emission rates, etc will be available only after completion of the experiments mainly at the end of 1980.

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4

Ethanol: Manufacture and Applications

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The production of ethanol via fermentation is in many cases easier done than avoided. Few if any primitive tribes are without their alcohol beverages based on local sugars or starches, and residues from beer have been discovered in the Pyramids. Thus it is impossible to set a time when production of ethanol for beverage purposes began. Most alcohol in undeveloped countries is still for beverages. Aside from beverage production, ethanol (ethyl alcohol or "alcohol") is made for industrial purposes by both synthetic and fermentation processes.

Synthetic Alcohol Manufacture

The first synthetic ethanol was produced by a subsidiary of Union Carbide at South Charleston, West Virginia in the late 1920's; thus synthetic production is over 50 years old.

In the original process, ethylene gas was fed into strong sulfuric acid (around 90 per cent) at moderate temperatures and near atmospheric pressure. The ethylene was converted largely to ethyl hydrogen sulfate, but partly to diethyl sulfate. Some polymerization of the ethylene also took place.

The rich acid was then diluted with water and the temperature raised, hydrolyzing the esters and driving off the alcohol thus produced, along with ethyl ether and the lower boiling polymers.

The dilute acid was then concentrated at atmospheric pressure, producing a reusable acid but also a number of troublesome by-products. Sulfur trioxide vapor was produced as the acid became more concentrated. This produced an intolerable fog, so electrostatic precipitators were installed and the remaining vapor was decomposed by heat into sulfur dioxide which was discharged from a high stack.

Much of the polymerized ethylene could be removed from the weak acid by skimming and filtration, but a certain amount remained. This was partially oxidized by the acid during concentration, producing carbon dioxide and carbon; sulfur dioxide was another product of the concentration process.

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Vacuum concentration of the acid using Mantius, Swenson and other concentrators was used to some extent, but presented operational difficulties.

Although a patent was issued as early as 1936 covering aqueous phosphoric acid[1] the sulfuric acid ester process was unchallenged for nearly 20 years in spite of corrosion and pollution problems, but is no longer in much use.

Current synthetic production uses a weaker non-oxidizing acid. A respectable reaction rate requires higher temperatures, which shifts the equilibrium unfavorably, and high pressures. Typically, a reactor is operated using phosphoric acid on a porous carrier with a temperature around 250° C and a pressure of 70 bars. The Shell process uses granular silica gel, while Veba-Chemie (now part of Chemische Werke Huels) uses balls apparently made of clay which is leached after firing. The silica gel apparently produces more conversion per pass, while the Veba catalyst is far more durable. "Case hardening" of silica gel[2] greatly improves durability, and the Davison division of W. R. Grace & Co. has an experimental pelleted catalyst carrier based on silica gel which is claimed to be even better.

Typically, the hydration occurs using 0.3 - 0.5 moles water per mole ethylene and a space velocity around 1 min^{-1}, with 4 - 5 per cent conversion of ethylene per pass. The reaction is exothermic but because of low conversion the reacting mixture does not require cooling. Ether is produced but may be recycled if it is not wanted as a by-product.

Increased ethylene concentration or temperature produces more oils, butanes, carbon, etc., while more water dilutes the phosphoric acid and reduces its activity. Exact operating conditions will vary with the condition of the catalyst.

There is some loss of phosphoric acid into the product leaving the reactor in the form of an ethyl ester or perhaps as some species of phosphoric acid. It is replaced by either continously or intermittently adding makeup acid or by shutdowns and reimpregnation.

It is not impossible that other acids could be used instead of phosphoric. One would look for an extremely non-volatile acid, probably a transition metal oxide with good resistance to reduction and low water solubility (to permit more water in the feed). One producer may be using such an acid.

Following reaction, the ethylene gas is scrubbed to remove the alcohol and more or less of the ether and is then recycled. A side stream is purified, vented, or used in another process.

A crude synthetic alcohol is obtained at 15 - 30 per cent alcohol and contains acetaldehyde, oils, butanols, ether and some dissolved C_4 - C_6 hydrocarbons along with ethylene. It is distilled to remove low and high-boiling impurities and to concentrate to 190 proof. Details of the distillation are often proprietary. A good "spirits" grade of synthetic alcohol is at least as pure as the best fermentation alcohol.

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Small amounts of synthetic alcohol occur as by-products in various chemical processes, particularly production of acetic acid via butane oxidation. One company is producing about 12 million gallons of by-product ethanol at present but is not recovering it.[3]

Fermentation Alcohol Manufacture

United States capacity for fermentation industrial ethanol is estimated at 80 - 90 million gallons per year but this could be increased by diversion of distilled beverage production. About 10 million gallons of the fermentation alcohol is derived from wastes such as sulfite liquor or whey, but the balance presently depends on damaged grain or sugar, crop surpluses and molasses. Relative costs of ethylene and carbohydrates will change this in a few years, but no reversal to ethanol-based ethylene is likely in this country for much longer, perhaps through 1990.[4]

There is curently a government-sponsored program to increase fermentation alcohol capacity to provide material for gasohol. The issues here are numerous and complex, and emotionally-colored evaluations are clearly evident even among those who profess to have purely scientific or technical interests. Barring a drastic rise in grain prices the program is likely to continue.

The basic process for fermentation alcohol is little changed over the last hundred years. Typically the grain is ground, slurried with water and cooked. The cooking process causes the starch granules to take in water, swell and eventually rupture. This releases the starch molecules into the mash as long chain dextrins which are in turn broken down by the action of a saccharifying enzyme to simple sugars. Yeast is added to the mixture, and the sugars are converted to alcohol and carbon dioxide. The fermented mash, now called beer, is stripped of its alcohol by distillation. The spent beer which consists of the non-fermentable portions of the grain is separated into two fractions, the solubles and insolubles. The soluble portion is evaporated to produce a syrup containing 35 - 50 per cent total solids. This can be marketed as is or dried with the insoluble portion to form distillers dried grains with solubles---DDGS. The insoluble fraction can be marketed wet or dried to form distillers dried grains---DDG. These by-products are usually sold as dairy ration supplements, especially the wet grains and whole stillage fractions.

Molasses fermentation is more straightforward, as the milling and saccharifying operations are not needed. The molasses is diluted to 15 - 20 per cent sugars, depending on conditions, fermented, distilled and the remainder evaporated to a syrup. However, this syrup can only be used in small proportions for

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feeding because of its high potassium content. Alfa-Laval[5] is promoting a process for reducing this potash level in the syrup and obtaining potassium for fertilizer use and return to the land.

The sulfite process for paper-making produces a certain amount of wood sugars which cannot be sewered because of pollution laws. Fermentation permits recovery of the sugar as alcohol and single cell protein. A commercial plant is in operation.

An economically ideal substrate for fermentation is cellulose. However, it is associated with lignin which inhibits hydrolysis of the cellulose to simple sugars. The earliest studies of ethanol production via hydrolysis of cellulose were carried out in Germany during World War I. At that time two proceses were developed; the weak acid Scholler process and the strong Rheinau technique. Studies on the enzymatic hydrolysis of cellulose were initiated during World War II to try to find a remedy for the microbiological degradation of soldiers' uniforms. However, it is only within the last ten years that a renewed interest in hydrolysis of cellulose has taken place and cellulase enzymes are now being developed.

Variations of acid hydrolysis processes are being investigated. Certain fungi, especially Trichoderma reesei, can also degrade cellulose to sugars. To date, most results of cellulose-type enzymatic degradations produce only low sugar concentrations (e.g. 50 - 60 per cent yield at 5 - 10 per cent glucose[6]).

The technology---though not the basic process---associated with fermentation has developed considerably over the last fifty years. One of the major breakthroughs was the Melle process for the reuse of yeast. This was developed by Les Usines de Melle[7] and incorporated the use of centrifuges to recover yeast from the beer prior to distillation. This yeast was in turn used to inoculate the next fermentor. The process has three major advantages:

1. the efficiency of fermentation increases, reaching the Pasteur theoretical,
2. fermentation takes place at a faster rate, and
3. the cost of yeast replacement is considerably reduced.

The acclimation of the yeast cells to the particluar substrate combined with the large numbers account for the first two advantages, and the third can be costed out on the basis of yeast cost versus purchase and operation of centrifuges.

Cell recovery is mainly concerned with what is known as clear mash, i.e. sugar solutions without any entrained solids suchas as those in a whole-grain mash. The use of cell recovery on mash can be accomplished by clarifying the mash prior to fermentation or else incorporating a wet-milling front end and taking the saccharified starch as substrate. However the production of a clear mash directly from cereal mash is presently not feasible. This is due to excessive losses of carbohydrate in the cake or non-fermentable extract ranging from 10 to 20 per

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cent of total starch. This cake even, with a higher carbohydrate content than DDG, is not as valuable as DDG because of its lower protein concentration.

Taking the idea of yeast recovery one step further is continuous fermentation. This incorporates a vessel or vessels inoculated with yeast through which the fermentable substrate is passed continuously. The flow is designed to ensure that all the sugar is fermented before it exits the final fermenter as beer. This beer is clarified to remove any entrained yeast cells and a percentage of the yeast is recycled back into the system. The excess can be further processed depending on the market application, i.e. for human or animal use.

A great amount of time, money and effort is being devoted to the use of cellulose as a feedstock for the production of ethanol. The studies incorporate chemical or enzymatic conversion of the cellulose to glucose and the conversion of this to ethanol with yeast (Saccharomyces) or bacteria (Zymomonas). However, a third process is presently under development at Massachusetts Institute of Technology whereby the direct conversion of cellulose to ethanol is being attempted without a separate hydrolysis step.[8] This is accomplished by utilizing two separate microorganisms which work symbiotically with each other, Clostridium thermocellum and Clostridium thermosaccharolyticum to produce ethanol. The research is still in its infancy and several years of research and development are anticipated before its use commercially.

Within the last ten years phenomenal advances in the field of genetic engineering have taken place. It is hoped, but not yet demonstrated, that gene splicing may lead to major advances in the production of alcohol, but carefully controlled use of conventional microorganisms is now the best potential route to good economics.

Applications

Synthetic alcohol demand in the United States in 1979 was estimated at 208 million gallons (190 proof).[9] The same source lists 94 million gallons for chemical manufacture, 42 million for toiletries and cosmetics, 25 million for detergents, flavors and disinfectants, 23 million for coatings and 25 million for other uses. Synthetic alcohol is not used in beverages or gasohol (motor fuel).

Fermentation alcohol has been used almost entirely for beverage purposes in less developed countries. In industrialized nations, even with available ethylene, fermentation alcohol is produced from low-cost surplus and waste materials. With the shift in economics it will compete with synthetic in the latter's fields. It has a monopoly of "gasohol" for political reasons and of beverages for emotional reasons. Fermentation alcohol capacity in the United States is uncertain but is estimated at

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about 100 million gallons per year apart from beverages (65 million gallons produced in 1978---capacity not available).

As many as 70 products were at one time produced commercially from ethanol. Some of these downstream products are butanol, 2-ethyl hexanol, crotonaldehyde, butyraldehyde, acetaldehyde, acetic acid, butadiene, sorbic acid, 2-ethylbutanol, ethyl ether, many esters, ethanol-glycol ethers, acetic anhydride, vinyl acetate, ethyl vinyl ether, even ethylene gas. Many of these products are now more economically made from other feedstocks such as ethylene for acetaldehyde and methanol-carbon monoxide for acetic acid. Time will tell when a revival of biologically-oriented processes will offer lower-cost routes to at least the simpler products.

Recent Developments

The outstanding recent development in ethyl alcohol is "gasohol", a blend of fermentation ethanol (10 per cent) with gasoline. It was studied thoroughly about 50 years ago[10,11] but forced out by cheap oil. The alcohol must be nearly 200 proof, especially in cold areas. Apart from extending the petroleum supply directly, it permits use of lower-base octane gasoline and thus indirectly further increases the yield of gasoline per barrel of crude oil. Cooler engine temperatures reduce engine wear and pollution. Views on gasohol are held, often quite emotionally, and split into two camps. The opponents claim the energy required to produce the alcohol is greater than the energy it contains. They ignore the fact that gasohol seems to give the same gas mileage as gasoline in spite of a lower Btu content per gallon and that gasoline itself is subject to the same criticism. Their energy values are suspect because existing distilleries' poor energy economics are a legacy of the age when energy was cheap; there has been no demand for better technology until recently. The proponents of gasohol are often oriented toward the agricultural benefits of increasing the demand for cereal grains and other fermentables. The middle ground is clearly to be preferred; some alcohol will be made for motor fuel out of economically available substrates, but we cannot realistically expect or demand that all motor fuel sold in this country have ten per cent fermentation alcohol based solely on foodstuffs.

Several suppliers of motor fuel are considering contracts and joint ventures with alcohol producers or building plants independently. One view would suspect the choice of positions may reflect a company's ability to produce premium unleaded gasoline in desired amounts or its crude-oil position.

A second recent development is increased interest in the conversion of cellulose to fermentable sugar for conversion to alcohol. The enzymatic conversion is thus far not well enough developed to be successful commercially, although break-

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throughs may come any day. This new interest has been spurred on by diminishing petroleum stocks and rising prices. It is envisaged that cellulose, the most abundant polysaccharide in nature, will fulfill part of our liquid fuel needs. Acid hydrolysis is feasible, in fact was practiced in Europe during World War II to provide motor fuel, but this route is now no more than marginally profitable. The readjustments of energy and raw material costs now taking place will inevitably bring about desirable technical developmetns including more favorable energy balances. Use of straight 190-proof alcohol (95 volume per cent) as an automobile fuel is being pushed in Brazil and may find a place in less temperate climates as well. The need for production of anhydrous alcohol for gasohol has stimulated a search for new methods to replace the conventional ternary azeotrope method based on benzene or cyclohexane. Adsorption and extractive distillation along with other azeotroping agents and operation at various pressures are also being mentioned.

Finally, it should be noted that commercial production of ethanol by continuous fermentation of grain mash has reportedly been achieved at Archer-Daniels-Midland Company and that National Distillers' researchers have also developed such a process. Although continuous fermentation, per se, is not new there is some skepticism concerning the degree to which this represents a real technical and economic advance.[12]

A few other comments: Ethanol is listed by OSHA as a suspect but unproved carcinogen, but OSHA does not have jurisdiction over beverage alcohol, nor, since it is a natural product, does the Delaney Amendment apply. This could lead to paradoxical situations. Ethanol will continue to grow explosively in volume in the next few years as a motor fuel; indeed, this has happened in Brazil. The field is extremely volatile, and new developments occur every week, particularly with respect to fermentation and gasohol. Things should be clearer in about five years, and we should remind ourselves to take a similar look at ethanol then.

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Ethanol in Motor Gasoline

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Transportation fuels derived by blending of biomass derived ethanol and gasoline offer immediate potential to significantly supplement petroleum derived fuels. Ethanol can supplement the supply of gasoline produced from foreign crude oil. Oil imports currently provide the raw material for production of half of the liquid fuels consumed in the U.S., and represent a cash outflow of almost $9 million per hour. Events in recent years have dramatically illustrated the substantial economic cost, supply vulnerability, and resulting economic instability resulting from the high degree of dependency on imported oil. Biomass derived ethanol offers an immediate method of reducing oil imports since it is one of a very limited number of alternative fuels that is likely to be available in significant quantity before 1985.

Alcohols fuels have been under detailed study in the United States, Brazil, West Germany and other countries. In the United States, evaluation of the use of ethanol as an automobile fuel dates back to the earliest years of automotive use. For example, the U.S. Department of Agriculture published a report in 1907 entitled "Use of Alcohol and Gasoline in Farm Engines"(1). Interest in ethanol from grain has continued to the present day. As an example, by late 1974 the Nebraska Agricultural Products Industrial Utilization Committee had started sponsorship of a gasoline-ethanol blend fleet testing program. Since the initial testing, a broad-based grass roots movement has developed to support the development of ethanol as a renewable alternative domestic liquid fuel.

Much recent attention and investigation has been focused on the use of ethanol as a gasoline extender, octane enhancer, or as an alternative fuel. Many studies have been performed to evaluate the engine performance, emission characteristics, and the advantages and problem areas encountered in conventional spark

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ignition engines when ethanol is used as a fuel. These studies have defined the performance of ethanol and gasoline in various proportion blends in conventional engines. Fleet testing of various blends is currently being performed. Gasohol, which is a mixture of 10 percent by volume anhydrous ethanol in 90 percent unleaded gasoline, has expanded to include more than 2000 outlets in 35 states.

On 11 January, 1980, the Administration announced an expanded alcohol fuels program which will provide substantial stimulus to accelerate domestic production of alcohol fuels from sources other than petroleum. A target was set for domestic production capability of 500 million gallons during 1981. If this amount of ethanol were all blended to make gasohol, gasohol would then account for almost 10 percent of our anticipated 1981 demand for unleaded gasoline or about one percent of total gasoline use. This represents approximately a six-fold increase over existing alcohol fuel production capacity. The program includes a variety of incentives, from tax credits to loan and loan gurantees, which focus on two main objectives:

- o First, to permit gasohol to become economically competitive with unleaded gasoline at the pump
- o Second, to stimulate new investment in facilities to produce ethanol

These initiatives are designed to greatly increase the use of gasohol in passenger and commercial vehicles, as well as to encourage increased use of alcohol as fuel for off-highway use, such as in farm equipment. Key elements of the expanded program include:

Permanent exemption for gasohol from the 4¢/gallon federal gasoline excise tax. The President originally proposed an exemption of gasohol from the 4¢/gallon federal excise tax in 1977. In November 1978, the current exemption which expires in 1984 was signed into law. In April 1979, the Administration proposed that the exemption be made permanent in order to provide a long-term incentive which investors in ethanol plants can count on over the life of their facilities.

The Senate version of the Windfall Profits Tax bill would extend the exemption to the year 2000. This exemption provides a subsidy equal to 40¢ per gallon of ethanol. In concert with the tax credit discussed below, it is the most important incentive available to accelerate alcohol production and use.

40¢/gallon production tax credit. The Administration supports the establishment of a tax credit for producers who use the alcohol directly without blending with gasoline. This use is expected to occur mainly on farms. The Senate version of the Windfall Profits Tax bill would provide a production tax credit of 40¢/gallon for alcohol over 190 proof, 30¢/gallon for alcohol from 150 to 190 proof.

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$3 billion federal credit program. A $3 billion, ten-year program of loans and loan guarantees for construction of small and medium-scale alcohol and other biomass production facilities has also been proposed. The smaller facilities would be located mainly on individual farms for use in farm equipment. This program will also assist farmer cooperatives for the production of alcohol for either on-farm or commercial use. In general, plants eligible for this assistance will produce less than 30 million gallons per year, with most facilities located on farms producing less than 5 million gallons per year. Funding for this program would be authorized at an annual level of $300 million, $250 million for loan guarantees and $50 million for loans, and will be administered through the Departments of Agriculture and Energy.

Energy Security Corporation programs for biomass. The Administration supports the allocation of up to $1 billion of assistance available through the proposed Energy Security Corporation for the construction of plants for the production of ethanol from biomass. The ESC will have a number of financing tools, including loans, loan guarantees, price guarantees and purchase agreements to encourage private investment in facilities with significant potential to reduce imports. The Senate bill, S. 932, includes such a provision and prompt Conference Committee action on this legislation is expected.

Revision of the entitlements program. The Department of Energy has revised the crude oil entitlements program to include ethanol produced from biomass. This provides an incentive currently equal to about 5¢ per gallon of ethanol used in gasohol. Since the entitlement program phases out along with crude oil price controls -- ending on September 30, 1981 -- this program offers its benefits to those who begin production soon, thereby accelerating our near-term use of gasohol.

10% investment tax credit. The Energy Tax Act of 1978 authorizes a 10% additional investment tax credit for equipment to produce liquids or gases from biomass sources including the production of alcohol. This tax credit is in addition to the existing 10% investment tax credit, for which alcohol production facilities are also eligible. Under current law this credit will expire in 1982.

Alcohol production research and development. The Department of Agriculture and the Department of Energy administer research and development programs to improve our methods for producing alcohol fuels from biomass and to broaden the range of biomass products which can be used to make alcohol. In FY 1980, a total of over $30 million is dedicated to this effort. This R&D is important for improving the competitive viability of alcohol fuels as well as the net energy balance.

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500 million gallon target. The President announced a national target for alcohol production capacity -- 500 million gallons annually during 1981. Substantial amounts of alcohol will probably be burned directly, particularly for on-farm uses, rather than used for gasohol for commercial sale.

Today, without incentives, production of ethanol is not economically attractive when compared to gasoline, although rising world oil prices continue to improve the economics of gasohol. Net production costs for ethanol (after credits for sale of by-products) are approximately $1.30 per gallon compared to wholesale unleaded gasoline prices of $0.85 - $0.95 per gallon. (Jan. 1980 values). With the various federal subsidies in place, however, it is expected that an equivalent federal subsidy of almost $0.50 per gallon of alcohol will be available to producers. With this program combined with subsidies already available in over half of the states, the resulting economics for ethanol production are even further improved.

Ethanol Fuels Policy Issues

Existing and proposed federal and state incentives for fermentation ethanol production and use have contributed to the rapid expansion of the gasohol market. In addition, a broad spectrum of options is currently being pursued at the federal level to help accelerate the commercialization of gasohol by stimulating both its production and uses. Maximizing ethanol production will require a mix of various sized ethanol plants. Because of the lead time involved in building and operating larger facilities, the Department of Energy and the Solar Energy Research Institute (SERI) have produced a guide to provide basic information to individuals interested in constructing small-scale facilities (2).

Several policy issues must be addressed when considering production of significant quantities of ethanol for automotive fuel use; these include:

- o The potential near-term demand for biomass-derived ethanol
- o The availability of raw material feed for ethanol production, and the degree to which ethanol fuel production would infringe on food production
- o The overall ethanol production economics, including sensitivity to such factors as the cost of raw feed material, scale of production, and co-product credits
- o the effect of state and federal incentives on the production economics
- o The net energy gain achieved when producing ethanol
- o The environmental impacts of ethanol fuel production and the automotive emission characteristics of ethanol-gasoline blends

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Potential Demand for Biomass Derived Ethanol, 1980-1995. Review of annual gasoline demand for use in passenger cars and projected demands from various sources (3,4) indicate continuing strong demand for gasoline through the 1980-1995 period as shown in Figure 1. The reduced automotive consumption of gasoline, resulting primarily from Corporate Average Fuel Economy (CAFE) standards imposed on automobile manufacturers, will reduce annual gasoline demand during the 1980-1990 period. After 1990, the growth in the total number of automobiles will again become the predominant effect and overall passenger car gasoline demand will rise. In the near-term the level of imported oil will remain high, and ethanol blended with gasoline will continue to offer a method of reducing substantial oil imports.

Availability of Feedstocks. In the long term, if ethanol fuel conversion capacity exceeds levels readily sustained from surplus and distressed grains, and if cellulose-to-ethanol or coal-to-methanol technology should be slow to develop and be built, then it may be worth considering the encouragement of additional crops (including energy crops, such as sweet sorghum, which need not compete with food, feed, and fiber) or the use of set-aside acreage for alcohol crop production. It appears that an upper limit of approximately 3.3 billion gallons per year (216,000 barrels per day) of ethanol could be produced from raw material supplies using existing technologies, if conversion capacity capable of processing these feedstocks existed (5). The contribution of various agricultural commodities is shown in Table I. This limit could be achieved by bringing into production all existing grain land and by supplementing food processing by-products with sugar surpluses. However, achieving this limit would be expensive, and would reduce the flexibility of U.S. agricultural land and restrict options for food production. This table shows the quantity of ethanol which could be produced if: (a) USDA eliminates all future set-aside and diversion programs, and all existing grain land is brought into productive use; (b) cane sugar surpluses are converted to ethanol, (c) no new or marginal cropland is assumed to be brought into production, and sweet sorghum potential is not included.

Grain Alcohol Fuels Process Economics. As of late 1978, the posted price by refiners and operators for unleaded regular gasoline was in the range of \$0.45-0.50 per gallon. During the same period, the production cost of ethanol from corn was estimated to be from \$1.05-1.16 (\$1978). This would yield a discounted cash flow rate of return of 15-20 percent with corn feed cost of \$2.30 per bushel and a by-product credit of \$110 per ton of distiller's dried grains. From December 1978 to December 1979, the price of gasoline had increased dramatically from \$0.45-0.50 per gallon to the range of \$0.70-0.85 per gallon.

While the cost of producing ethanol has undoubtedly increased during the past year due to increased capital and operating expense, the price differential between unleaded

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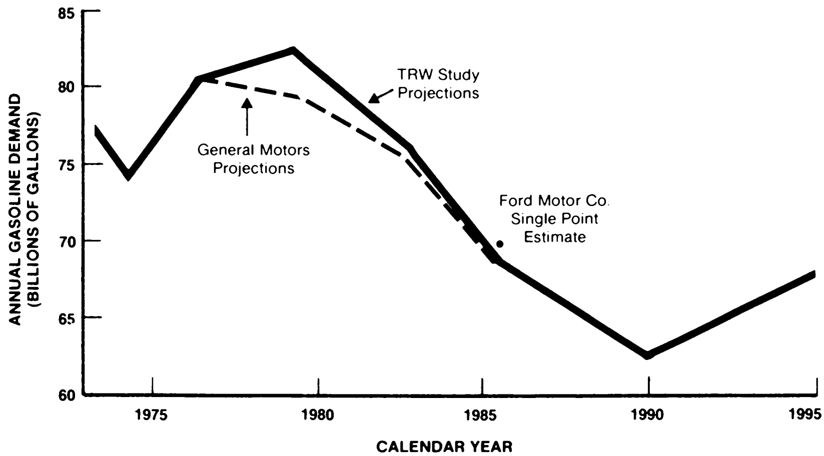

Figure 1. Comparison of annual gasoline demand projections for passengers cars to 1995

regular gasoline and grain ethanol motor fuel has narrowed dramatically in recent months. Grain ethanol fuel is becoming increasingly cost competitive as the price of gasoline continues to rise at a rate greater than general inflation.

Existing analyses indicate that the production cost of grain ethanol has a high degree of sensitivity to the cost of grain feedstock and the credits claimed for by-products such as the distiller's dried grain (6,7). As a rough guide, the cost per gallon of ethanol must rise 12 cents for each 10 percent increase in corn purchase price. Further, the cost per gallon could be reduced 4 cents for an increase of 10 percent in the by-product credit for distiller's dried grain. These approximate numbers assume a new 50 million gallon per year ethanol plant with a 20-year life requiring an investment of $58 million (1978) at 20 percent return on investment.

Federal and State Subsidies. The large increase in demand for gasohol is believed to be based, at least to some degree, on consumer preference for vehicle fuel derived from renewable resources, and the perception of the fuel as a high quality motor fuel. In addition, increased demand has occurred because grain ethanol for use in gasohol fuel mixtures has been made cost competitive with unleaded gasoline through state and federal price incentives. Alcohol fuels currently receive a wide range of federal and state government incentives. These incentives substantially improve the cost competitive position of grain ethanol when used in gasohol, relative to unleaded gasoline. These incentives as summarized in Table II include:

- The National Energy Act motor fuel excise tax exemption which applies through 1984 to gasoline/alcohol blends. This exemption is worth $.04 per gallon of gasoline/alcohol blend, or $0.40 per gallon or $16.80 per barrel of alcohol in 10 percent blends. The exemption does not apply to alcohol which uses petroleum, natural gas or coal as a feedstock. Some states have also exempted these blends from State excise taxes.
- Eligibility of alcohol fuels for Department of Energy entitlements, worth roughly 5 cents per gallon.
- Loan guarantees for alcohol pilot plants, administered through the U.S. Department of Agriculture, the Department of Housing and Urban Development, the Small Business Administration, the Economic Development Administration and Department of Energy.
- An additional 10 percent investment tax credit on top of the current 10 percent base. The value in Table II is based on a new 50 million gallon per year ethanol plant with a 20-year plant life and investment of $58 million (1978).

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Table I. Biomass Feedstocks Potentially Available for Ethanol Fuel Production

BIOMASS FEEDSTOCK	MATERIAL POTENTIALLY AVAILABLE FOR ETHANOL PRODUCTION		PRODUCTION POTENTIAL, MILLION GALLONS PER YEAR ETHANOL
	MILLION DRY TONS	MILLION BUSHELS	
Cheese Whey	0.9	—	90
Corn	16.0	640	1,660
Grain Sorghum	2.7	110	280
Sugar Cane	2.6	—	150
Wheat	11.4	420	1,130
TOTAL			3,310

Table II. Impact of Incentives Cost of Alcohol Used in Gasohol

	SUBSIDY (Dollars)		EFFECTIVE NET PRICE (Dollars)	
	PER GALLON OF ALCOHOL	PER BARREL OF ALCOHOL	PER GALLON OF ALCOHOL	PER BARREL OF ALCOHOL
Base: Market Price (Dec. 1979) of ethanol used in gasohol			1.62	68.04
Subsidy:				
1. Exemption of Federal excise tax ($0.04 per gallon of fuel containing 10 percent alcohol	0.40	16.80	1.22	51.24
2. 20 percent investment tax credit	0.01	0.42	1.21	50.82
3. Entitlement credit (approximately $0.05 per gallon of ethanol)	0.05	2.10	1.16	48.72
4. State Incentive: Rebate of State Tax on Gasoline:				
Arkansas	0.95	39.90	0.21	8.82
California	0.50	21.00	0.66	27.72
Colorado	0.50	21.00	0.66	27.72
Connecticut	0.10	4.20	1.06	44.52
Indiana	0.32	13.44	0.84	35.28
Iowa	0.65	27.30	0.51	21.42
Kansas	0.50	21.00	0.66	27.72
Louisiana	0.80	33.60	0.36	15.12
Maryland	0.10	4.20	1.06	44.52
Montana	0.70	29.40	0.46	19.32
Nebraska	0.50	21.00	0.66	27.72
New Hampshire	0.50	21.00	0.66	27.72
North Dakota	0.40	16.80	0.76	31.92
Oklahoma	0.65	27.30	0.51	21.42
South Dakota	0.40	16.80	0.76	31.92
Wyoming	0.40	16.80	0.76	31.92

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Net Energy Gain in Biomass Derived Ethanol Production. Numerous studies have examined the net energy balance issue of alcohol production and use. The majority conclude that the net balance is small but positive, but exact estimates differ, depending on the feedstock and process employed. It is expected that advances in technology and ability to utilize feedstock by-products more effectively will improve the net energy balance. For example, a plant using food processing residue for feedstock and coal for fuel may achieve a net reduction in imports approaching its total production. Also, the use of coal in the alcohol production process improves the oil savings attainable through increased use of gasohol. Thus, the use of coal or renewable fuels such as wood, agricultural residues, geothermal energy or solar energy for alcohol production is highly preferable to use of oil or natural gas.

Ethanol conversion facilities can readily be designed to use fuel sources other than oil or natural gas. Small-scale on farm plants can utilize corn stover as a boiler fuel, and larger plants can rely on coal as a boiler fuel to produce process steam. The ethanol production process can then be viewed as a means of converting lower grade energy forms, such as coal, distressed crops or solar energy, into premium transportation fuel.

Environmental Effects of Ethanol Production. Production of ethanol could potentially produce two forms of air pollution: the release of pollutants from the boiler used to produce process steam, and vaporization of ethanol during the production process. If crop residues or lower grade fuels such as coal (low sulfur) are used as boiler fuel, which is preferable from a net energy gain basis, the resulting pollutants may be controlled through use of flue gas stack scrubbers. The release of ethanol vapors at the plant site is not considered a major concern at this time.

In small-scale farm production of ethanol a possible environmental impact could occur through removal of crop residues for use as a boiler fuel. Crop residues are important because they help control soil erosion through their cover and provide nutrients, minerals, and fibrous material which help maintain soil quality. However, not more than one-third to one-half of the residues from a grain crop devoted to ethanol production need be used to fuel the process. Also, there are several methods, such as crop rotation and winter cover crops, which lessen the impact of crop residue removal.

A second environmental impact which might occur is related to the application of thin stillage to the land. Thin stillage, a product of the grain fermentation filtering process is composed of very small solid particles and solubles. Two kinds of problems can result from applying thin stillage to the land: odor and acidity. The impacts of applying thin stillage to the land

can be attenuated by using a sludge plow, possible recycling of the thin stillage within the plant, or use of anaerobic digestion to reduce the pollution potential of the thin stillage.

Technical Aspects of the Use of Ethanol-Gasoline Blends in Spark Ignition Engines

Consideration of the large scale use of ethanol-gasoline blends in conventional gasoline spark ignition engines requires evaluation of several key technical issues. In particular, in blends with high proportions of ethanol, the characteristics and performance may change substantially from the properties of gasoline. Evaluation of ethanol-gasoline blends, including gasohol have focused on the following technical areas:

- The relative differences in chemical and physical properties of ethanol, gasoline, and ethanol-gasoline blends
- The performance of ethanol-gasoline blends and ethanol in conventional spark ignition engines
- Effect of ethanol-gasoline blends on engine emissions
- The compatibility of ethanol-gasoline blends with automotive fuel and engine systems

Chemical and Physical Properties of Ethanol and Gasoline. The differing performance of ethanol and ethanol-gasoline blends in conventional spark ignition engines compared to straight gasoline can be attributed to the differences in chemical and physical properties. While gasoline is a mixture of about 4 to 12 carbon atom hydrocarbons, ethanol is a single compound with uniquely and narrowly defined properties. Differences in engine performance and system compatibility between gasoline, ethanol, and ethanol blends can be attributed predominantly to flash point, boiling point, octane quality, heat of vaporization, heating value, stoichiometric air/fuel ratio required for combustion, and water solubility. As a greater percentage of ethanol is added to straight gasoline, the deviation of characteristics is approximately proportional to the percentage of ethanol.

The octane-boosting properties of ethanol in gasoline were particularly attractive at a time when higher octane lead-free gasolines were in short supply and other octane enhancers such as MMT (methylcyclopentadienyl manganese tricarbonyl) and lead are under restrictions. For example, a three percent ethanol addition increases typical gasoline octane (measured as the average of "research" and "motor" octane) by roughly one point. In a gasohol mixture, the addition of 10 percent ethanol increases the octane by 2 to 3 points depending on the composition of the gasoline. Ethanol has been permitted by the Environmental Protection Agency for use as a gasoline additive under Section

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211(f) of the Clean Air Act. Two other chemicals - TBA (tertiary butyl alcohol) and MTBE (methyl tertiary butyl ether) also have been permitted as octane enhancers. However, both are currently made largely from petroleum.

Performance of Ethanol-Gasoline Blends in Spark Ignition Engines. A number of gasohol fleet tests have been run to evaluate performance under normal driving conditions. In addition, a number of authors have compiled technical information or performed laboratory and performance tests to evaluate various proportional blends of gasoline and ethanol (8,9,10). The gasohol fleet tests performed so far, have not been performed under the degree of rigorous controls and testing procedures that would ensure complete accuracy. However, none of the fleet testing which has been performed indicates any major problems with the use of gasohol in normal automotive use. The Department of Energy has received the results of extensive tests conducted by the state governments of Illinois, Nebraska and Iowa and also by the American Automobile Association. These tests indicate that the great majority of unmodified vehicles tested ran as well or better with gasohol than with fuel previously used. Specifically,

- The American Automobile Association test showed that 88% of the vehicles ran as well or better on gasohol, which suggests that 12% of the vehicles showed negative results and would require some minor modification for comparable or improved performance on gasohol.
- Illinois state government officials indicate that their test, (began in June 1978 and continuing beyond the date of this paper) which has used approximately 1,800 state vehicles including state police cars, has yielded positive results in each category tested.
- The Iowa Development Commission (a state agency) conducted a 90 day gasohol marketing (customer opinion) test from June 15, 1978 to September 15, 1978, in which 232,000 gallons of gasohol were sold at five stations (also offering unleaded regular) across the state. Results show: a) 67% of users reported improved performance (29% cited increased mileage), b) three of every five users were repeat customers, c) 90% of users would purchase gasohol if it were available at most stations, d) gasohol outsold unleaded regular 3.9 to 1.

Gasohol is being used in automobiles without modification. With normal precautions to maintain a moisture free blend during refining/mixing, transportation, and at the service station, the tendency of the ethanol-gasoline mixture to undergo phase separation can be minimized. The presence of alcohol in the gasoline increases the water tolerance of the gasoline. While only a maximum of a few parts per million of water will mix freely with gasoline, a gasohol mixture will tolerate nearly 0.25 percent

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water (depending on temperature) before phase separation takes place. Because most automobiles have some small percentage of water in their gas tanks, the use of anhydrous ethanol will minimize phase separation problems.

Certain minor driveability problems can occur when using ethanol-gasoline blends in engines which are set-up for optimum performance with gasoline. With gasohol, under certain conditions, driveability problems may include:

- o Greater tendency of stalling and stumbling during engine warm-up
- o Increased tendency towards hesitation during acceleration for late model cars
- o Increased vapor lock tendency in hot climates or at high altitude

Leaning of the air/fuel ratio in a gasoline engine is known to impair driveability. Driveability problems resulting from a lean air fuel mixture can include increased engine stalling and stumbling during engine warm-up, increased tendency to hesitate during acceleration, and increased tendency for engine surge during constant speed driving. The use of ethanol in automotive fuel leans the air/fuel mixture because the ethanol molecule contains oxygen, and increases the oxygen content in the engine combustion chamber. In late model vehicles which are adjusted to run lean in order to minimize pollution, the further leaning induced by use of blends can cause driveability problems. The same tendency is not typically present with older vehicles which have a richer initial air/fuel ratio.

A quantitative measure of warm-up driveability is presented in the test results of Figure 2. The results of these limited tests indicated that the use of a 10 percent by volume ethanol blend can be expected to degrade warm-up driveability of standard (i.e., non-adjusted and non-modified) carbureted cars to a degree ranging from negligible to pronounced (8). Further, at 22 percent ethanol, warm-up driveability was degraded significantly in all three cars tested. The three cars were tested by a procedure which measures driveability with a Total Weighted Demerit (TWD) value. (Higher values of TWD indicate poorer engine driveability). Carburetor modifications performed to achieve an air/fuel ratio for the blend which is equivalent to straight gasoline will result in improved driveability.

For engines which are adjusted or modified to operate at equivalent air/fuel ratios, the fuel economy differences between gasohol and gasoline are apparently negligible. However, the leaning effect of ethanol may result in fuel economy or exhaust emissions effects ranging from significant increases to significant decreases, depending on the adjustment of the engine. An analysis of state and private test data received by DOE indicates that use of a 90/10 blend of unleaded regular gasoline and ethanol (compared to 100% unleaded regular) resulted in similar

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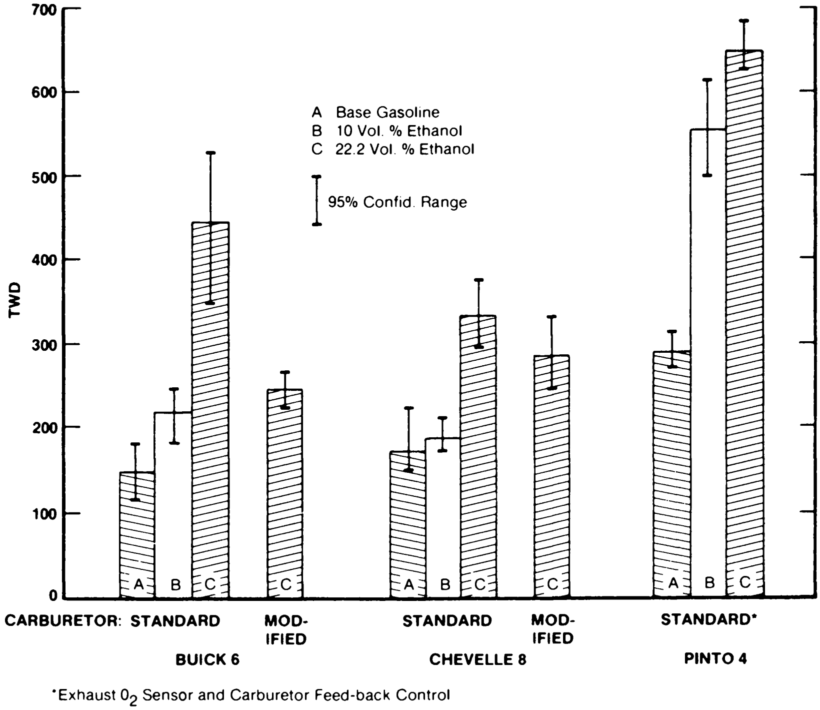

Figure 2. Warm-up driveability in three cars with gasoline and gasoline blends

miles per gallon or a small increase in mileage by a majority of the vehicles tested. A substantial mileage increase or decrease was found with a very few vehicles. Differing results in mileage are attributable to the differing age, size, condition and adjustment, weather conditions, and the differing quality of ethanol and gasoline employed.

Effect of the Use of Ethanol Gasoline Blends on Engine Emissions. On December 16, 1979, EPA approved use of gasohol under Section 211(f)(3) of the Clean Air Act of 1977 and found that there was no significant environmental risk associated with the continued use of gasohol. Furthermore, new emissions control systems, such as the "threeway catalyst with exhaust oxygen sensors for carburetion feedback for air-fuel control," have been shown to be equally effective using either gasoline or gasohol.

EPA and the Department of Energy have conducted a cooperative gasohol testing program to obtain and evaluate environmental impact data. On the basis of these tests, EPA concluded that the addition of 10% ethanol to gasoline (11):

- o slightly decreases hydrocarbon emissions
- o significantly decreases carbon monoxide emissions
- o slightly increases nitrogen oxides emissions
- o substantially increases evaporative hydrocarbon emissions

The results to date have been generally favorable with respect to the use of gasohol in automobiles. However, in a recent technical memorandum, the Office of Technology Assessment of the Congress of the United States stated that the "mixture of observed emissions reductions and increases, and the lack of extensive and controlled emissions testing, does not justify a strong value judgment about the environmental effect of gasohol used in the general automobile population (although the majority of analysts have concluded that the net effect is unlikely to be significant)"(12).

Compatibility of Ethanol-Gasoline Blends with Automotive Fuel/Engine Systems. Experience with gasohol has indicated that the solvent properties of ethanol loosen corrosion and dirt from the walls of fuel tanks and fuel lines of automobiles. This makes it advisable to flush and dry all storage tanks used with ethanol-gasoline blends. Vehicle tanks, particularly with older vehicles, should be flushed with ethanol or gasohol, and the fuel filter may require replacement after the first or second tankful. The use of neat ethanol or ethanol blends may potentially cause minor problems with corrosion of metal fuel system materials, particularly aluminum, copper, iron, lead and zinc. In addition, clear polyamid, used in fuel systems for such items as fuel filter housings, has been reported to fail in service with ethanol blends.

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Conclusions

Several considerations in the use of gasohol or ethanol-gasoline blends will ensure wide-scale application and maximum benefits to the United States:

- Small and large-scale production of ethanol should be expanded utilizing existing food crop surpluses as well as distressed grains.
- Ethanol plants should rely on lower utility fuel sources rather than premium fuels such as natural gas or petroleum derived fuels. Lower utility fuels may include coal, and renewable resources such as agricultural wastes (corn stover, bagasse) geothermal or solar energy.
- Phase separation of ethanol-gasoline blends resulting from blend water content dictates the use of anhydrous ethanol and that the blend distribution system exercise additional care to minimize water contamination
- The differences in fuel economy and exhaust emissions between a gasohol-type blend and straight gasoline are attributable to ethanol changing the effective air/fuel ratio of standard engines. Equal performance can be achieved by adjusting the air/fuel ratio to the equivalent value obtained with gasoline.
- Research, development and testing should continue to:
  - Identify new feedstocks with high alcohol yields
  - Accelerate the development of feedstock collection and conversion technologies capable of using low-cost, waste feedstocks (including cellulosic materials).
  - Resolve the fuel consumption and exhaust emission impacts of ethanol-gasoline blends.
  - Remove the technical and material constraints to the use of alcohol fuels in all highway and non-highway systems including diesel engines, turbines and on-farm uses.

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Manufacture of *n*-Butanol and 2-Ethylhexanol by the Rhodium Oxo Process and Applications of the Alcohols

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The oxo process consists of the reaction between an olefin, carbon monoxide, and hydrogen, in the presence of a catalyst (rhodium or cobalt) to form an aldehyde with one more carbon atom than the starting olefin.

$$R\text{-}CH{=}CH_2 + CO + H_2 \xrightarrow{\text{Catalyst}} R\text{-}CH_2\text{-}CH_2CHO$$

The only exception is with the cobalt catalyst when the starting olefin is ethylene, in which case both the aldehyde and diethyl ketone are formed.

The discovery of the oxo (or more accurately, hydroformylation) process was by Ruhrchemie's Roelen who applied for a German patent in 1938. This turned out to be a breakthrough method for both higher and lower alcohols production from the aldehydes. Exploitation of the process, however, was delayed by World War II. It was not until 1948 that commercialization occurred with the manufacture of isooctyl alcohol by Enjay Chemical Company (1).

Subsequently, a whole host of both lower (C_3, C_4, C_5) and higher (C_6, C_7, C_9, C_{10}, C_{11}, etc.) oxo alcohols have been commercialized. Of all these alcohols, the most important by far have turned out to be n-butanol and 2-ethylhexanol - both of which are derived from n-butyraldehyde based on hydroformylation of propylene. In addition to n-butyraldehyde, the lower valued isobutyraldehyde is produced as a by-product. Some of this is converted to isobutanol.

Propylene Oxonation Processes

There are three commercially significant oxo processes starting with propylene for the production of butanols and 2-ethylhexanol. The primary difference in these processes is associated with the catalyst system used to produce butyraldehyde. The catalysts are:

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TABLE I

Comparison of Processes for Propylene Oxonation

	Conventional Cobalt	Cobalt Ligand	Rhodium Ligand
Operating Pressure	High	Medium	Low
Operating Temperature	Medium	Medium	Low
Catalyst Cycle	Complex	Complex	Simple
n/i Isomer Ratio	3/1	9/1	≥10/1
Primary Product	Aldehydes	Alcohols	Aldehydes
Other By-Products	High	Medium	Low

In Monohydric Alcohols; Wickson, E.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1981.

- o conventional cobalt
- o cobalt ligand
- o rhodium ligand

Each catalyst system employs a unique set of operating conditions. A brief comparison of the three processes is shown in Table I.

With the conventional cobalt carbonyl catalyst, the ratio of n- to isobutyraldehyde produced is between 3 and 4:1. This low ratio represents a significant loss of propylene and synthesis gas (20-25%) to the lower valued or unwanted isobutyraldehyde. In lieu of having large and expensive storage facilities, isobutyraldehyde or isobutanol is frequently burned for fuel value. An alternative to burning is the expensive catalytic cracking of isobutyraldehyde to form synthesis gas and propylene for recycle and consumption in the hydroformylation step (2).

Considerable effort over the years has been devoted to a search for new oxo catalysts. This has been motivated by a desire to minimize the less valuable isobutyraldehyde/alcohol and also to lower oxo reaction temperatures and the high pressures (3-4000 psi) associated with the conventional cobalt process for reduced capital investment and increased energy savings.

In the case of the cobalt ligand process, alcohols rather than aldehydes are the main products. While the cobalt ligand catalyst overcomes the isomer ratio disadvantage, it has only one-fifth the activity of the conventional cobalt catalyst. Even at temperatures of 180-200°C, space time yields remain lower than in the conventional cobalt process. At the elevated temperatures the cobalt ligand catalyst is a highly active hydrogenation catalyst that converts a significant portion (10%) of the propylene to propane and most of the butyraldehyde to butanol.

The rhodium ligand process, which will be discussed in greater detail in the following sections, operates at lower pressures and temperatures and overcomes the high by-product levels as well as the isomer ratio disadvantage of the conventional cobalt catalyst.

Rhodium Low Pressure Oxonation

Union Carbide, Johnson Matthey and Davy McKee have jointly developed a low pressure, two-step rhodium catalyzed process which takes place at around 110°C and 100-300 psi (3, 4). The rhodium complex $HRh(CO)(P\phi_3)_3$ is stable at typical reaction temperatures and pressures. The rhodium concentration in the reaction mix is usually around 0.02 wt%.

A summary of the key features of this rhodium catalyzed low pressure oxo (LPO) process is as follows:

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- o Low Pressure Operation - Use of a highly active rhodium catalyst allows operation at pressures of 300 psi and less, far lower than with cobalt catalyst.

- o Efficient Feedstock Utilization - Aldehyde normal to iso ratios of 10:1 or greater are achieved with consequent reduction in losses of propylene and synthesis gas to isobutyraldehyde. In addition, losses to propane are reduced to 2 percent or less and losses to heavy by-products are insignificant. Hydrogenation of butyraldehyde to butanol is virtually nil, leading to a simpler product mix and the absence of acetals.

- o Lower Temperature - The LPO process operates 45-85°C lower than cobalt oxo processes. This significantly reduces efficiency losses from trimerization of butyraldehyde and from other side reactions.

- o Simplicity - The cumbersome and corrosive catalyst recycle systems of many conventional cobalt oxo processes are avoided.

- o High Catalyst Productivity - The high catalyst productivity leads to a low rhodium inventory and low catalyst cost per pound of product.

- o Low Energy Requirements - The low process operating pressure means that synthesis gas compression can be avoided. The process involves little distillation for product or by-product, thereby minimizing steam requirements.

High concentrations of CO reduce alcohol and paraffin formation but lower the n/i ratio. Excess ligand, i.e., $P\phi_3$ that is not chemically bound to Rh, is maintained at around 5-8 wt% in the reaction mix to achieve a high ratio of normal to iso aldehydes.

Catalyst Description. The LPO catalyst is a triphenylphosphine modified carbonyl complex of rhodium. Triphenylphosphine, carbon monoxide, and hydrogen form labile bonds with rhodium. Exotic catalyst synthesis and complicated catalyst handling steps are avoided since the desired rhodium complex forms under reaction conditions. Early work showed that a variety of rhodium compounds might be charged initially to produce the catalyst. Final selection was made on the basis of high yield of the catalyst precursor from a commodity rhodium salt, low toxicity, and good stability to air, heat, light, and shock.

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The exact reaction mechanism is uncertain, but it is believed to be as shown in Figure 1. The proposed mechanism illustrates factors that provide selectivity to normal product.

The initial step is coordination of propylene with species A. Propylene complex B rearranges to the alkyl complex C, which undergoes CO insertion to form the acyl derivative D. Oxidative addition of hydrogen gives the dihydroacyl complex E. Finally, hydrogen is transferred to the acyl group. Butyraldehyde is formed along with the 4-coordinate species, F.

The presence of an excess of triphenylphosphine ligand L under the low pressure conditions favors high selectivity to normal aldehyde. The excess ligand suppresses dissociation of species A into one containing only a single phosphine ligand. By favoring the presence of species A, when olefin attacks, the steric effect of the two bulky triphenylphosphine ligands favors a high ratio of primary alkyl. If few triphenylphosphine ligands were present in the complex, a higher proportion of propylene would form secondary alkyl groups, giving more isoaldehyde.

n-Butanol Manufacture Using a Rhodium Catalyst for The Oxo Reaction

A simplified flow diagram of the rhodium catalyzed oxo process is shown in Figure 2 (3, 4, 5). The synthesis gas and propylene streams are first purified via proprietary solid-absorbent techniques to remove catalyst poisons such as hydrogen sulfide or carbonyl sulfide. Then they join with recycle gas, and the combined stream enters the base of the hydroformylation reactor through a distributor. Here, the rhodium-based catalyst is present in a homogeneous liquid phase, dissolved together with free triphenylphosphine in a mixture of butyraldehyde and heavy by-products from aldehyde trimerization.

These aldehyde-condensation products are solvents for the catalyst. This allows the unit to operate without need for other solvents and forestalls the need for a catalyst-recycle step.

Because of the high activity of the catalyst, only a low rhodium concentration of several hundred parts-per-million is needed. The triphenylphosphine level is kept much higher-typically several percent by weight.

Reaction temperatures typically are 80 to 120°C at pressures between 200 and 300 psi. Heat of reaction is taken out partly via vaporization of aldehydes into the overhead gas stream, and partly by circulating a coolant through coils inside the reactor.

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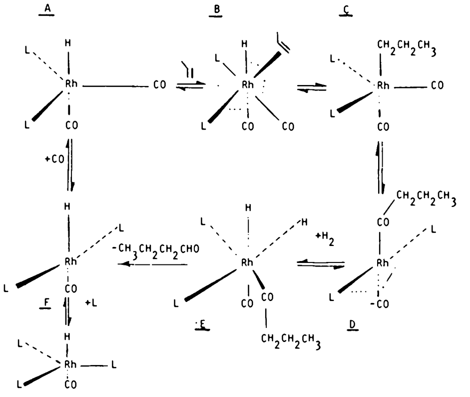

Figure 1. Possible catalyst mechanism

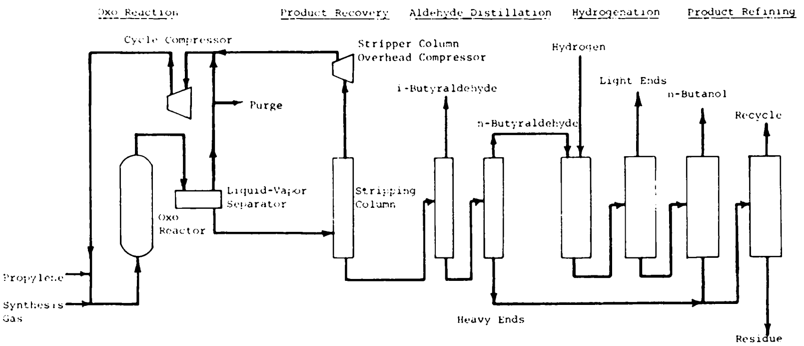

Figure 2. n-Butanol manufacture using a rhodium catalyst for the oxo reaction (3, 5)

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Reactor effluent is removed in the gaseous phase, passing through entrainment separators that minimize rhodium loss. This effluent then goes to a condenser where aldehydes and by-products drop out; this mixture is removed in a separator. The liquid stream from the separator contains appreciable amounts of dissolved gases, mainly propylene and propane. A product stripping column distills these out. The liquid stream from this stripper goes through two distillation columns in series that remove iso- and n-butyraldehyde as overhead products, respectively. A small stream that contains heavy by-products formed in the reactor leaves the bottom of the second column. This stream can be combined with the heavy ends stream from the n-butanol column and valuable aldehydes and alcohols recovered for recycle. The iso-butyraldehyde overhead product from the first aldehyde column may be hydrogenated and sold as a low cost solvent, cracked to synthesis gas and recycled to the oxo reactors, or burned as fuel.

The propylene-rich overhead product from the stripping column is compressed and recycled into the gas stream to the reactor. The overhead gas from the liquid-vapor separator likewise is compressed and recycled after a portion of it is bled off in a purge stream that controls the level of propane and other inert gases introduced with the feedstock in the gas circuit.

Butyraldehyde Hydrogenation and Refining. A wide variety of hydrogenation processes using copper, nickel or combined copper-nickel, fixed bed catalysts in either the vapor or liquid phase are used commercially (6, 7, 8, 9). After the hydrogenation step the butanol is refined using a two-column scheme. The first column removes water and a small amount of light ends produced during hydrogenation. The second column takes refined n-butanol as an overhead product. The small heavy ends stream from the second column is combined with the heavy ends stream from the n-butyraldehyde column for recovery and recycle of contained alcohols and aldehydes. The final residue stream is burned as fuel.

2-Ethylhexanol Manufacture Using A Rhodium Catalyst For The Oxo Reaction

The production of 2-ethylhexanol from propylene by the rhodium catalyzed, low pressure oxo process is accomplished in three chemical steps. The first step of the process (described in section on n-butanol manufacture) converts propylene to normal butyraldehyde by hydroformylation in the presence of a rhodium catalyst. In a second step, the normal aldehyde is aldoled to form 2-ethylhexenal. 2-Ethylhexenal is then hydrogenated to 2-ethylhexanol and refined in the third and final step (see Figure 3).

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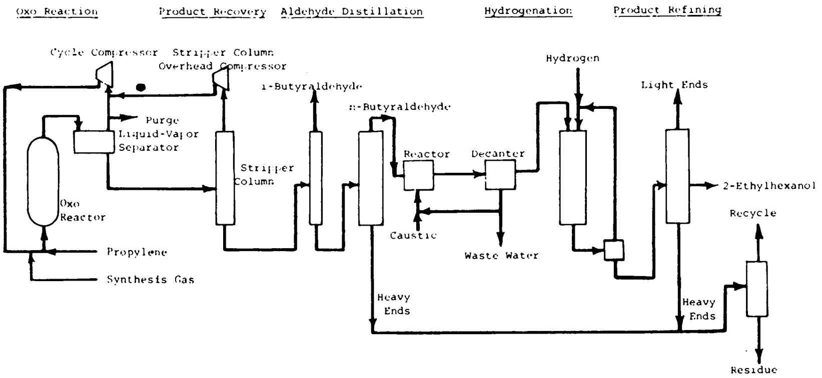

Figure 3. 2-Ethylhexanol manufacture using a rhodium catalyst for the oxo reaction (3, 5)

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Aldolization, Hydrogenation and Refining. In the second processing step, aldolization (10), n-butyraldehyde is added to aqueous sodium hydroxide which is recycled from the decanter. The caustic concentration in the cycle is maintained at 3% by adding makeup caustic. Residence time in the aldol reactor is typically about 60 seconds. Reaction temperature is controlled between 110°C and 120°C at pressures of 50 to 70 psi. The reactor effluent is fed to a decanter to separate the 2-ethylhexenal (EPA) from the caustic solution recycle. Water produced by dehydration of the aldol dilutes the cycle and is purged after decantation.

The third processing step receives the organic phase from the decanter for hydrogenation to 2-ethylhexanol. As in the case of butanols, the hydrogenation of EPA is accomplished by a wide variety of processes (6, 7, 8, 9). In the process shown in the flow diagram, EPA is vaporized into a recycle hydrogen stream and reacted over a copper or copper-nickel catalyst at 150° to 200°C at 50 to 70 psi. Crude 2-ethylhexanol is condensed from the hydrogen cycle and refined in a single column which takes water and light ends overhead and heavy ends as a tails stream. Refined 2-ethylhexanol is taken as a side stream make. Heavy ends from the n-butyraldehyde column and the 2EH column are fed to a second column to recover and recycle aldehydes and alcohols. The residue is burned as fuel.

Applications

The key industrial applications and markets for normal and isobutanol and 2-ethylhexanol are discussed . As will be noted, the C_4 oxo alcohols find use primarily within the coatings industry, either as solvents, per se, or as intermediates to manufacture solvents or protective coatings chemicals. Applications for 2-ethylhexanol, while numerous and varied, are basically oriented toward the manufacture of plasticizers for polyvinyl chloride. Total U.S. consumption of these alcohols in 1979 was approximately 1.3 billion pounds - 730 million pounds of n-butanol, 190 million pounds of isobutanol, and 380 million pounds of 2-ethylhexanol. The consumption pattern is summarized in Table II and described in the following sections:

n-Butanol. This alcohol is widely used as a solvent or co-solvent in industrial protective coatings formulations. It has traditionally been the preferred solvent or co-solvent in applications where slower drying is desired. The major segments of the n-butanol coatings solvent market are:

- nitrocellulose lacquers used as both top coats and sealers in wood finishing applications.

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Table II

n-Butanol, Isobutanol, 2-Ethylhexanol
Consumption Pattern - U.S.A.

End Use	Consumption Pattern, 1979 % of Total
n-Butanol	
Butyl Acrylate	27
Coatings Solvent	22
Butyl Glycol Ethers	22
Butyl Acetate	13
Plasticizers	8
Butyl Amines	2
Butyl Methacrylate	2
Lube Oil Additives	1
Miscellaneous	3
	100
Isobutanol	
Isobutylamines	32
Coatings Solvent	21
Isobutyl Acetate	16
Lube Oil Additives	13
Plasticizers	8
Miscellaneous	10
	100
2-Ethylhexanol	
Plasticizers	72
Acrylates	15
Oil and Fuel Additives	6
Surfactants	4
Miscellaneous	3
	100

- thermoset acrylic resin coating systems applied mainly in the metal furniture field, appliances, and coil coatings.

- acrylic-melamine resin coating systems (70% acrylic/30% melamine) used in the automotive refinishing and top coat markets where ease of application and low cost are prime considerations.

- amino resin systems such as alkyd-urea and alkyd-melamine.

- water-reducible coatings (as a co-solvent).

Coatings solvent applications account for approximately 22 percent of total n-butanol demand in the United States. The market is predicted to remain relatively stagnant over the next five years and then gradually decline as water-borne and other higher solids coatings systems are developed in response to the legislative and various socio-economic forces facing the coatings industry.

n-Butyl acrylate, made by esterification of the alcohol with acrylic acid, is a major application representing about 27 percent of n-butanol domestic demand. Acrylic coating resins based on n-butyl acrylate, ethyl acrylate, and methyl methacrylate established their position in the industrial coatings market during the early 1960's. These systems are widely used in auto top coats and coil and appliance coating applications. In the trade paint area, exterior house paints based on water-borne acrylic latexes have largely displaced oil-based alkyd systems in this market. n-Butyl acrylate is expected to grow at a rate of about 6 percent per year over the next five years.

Also in the acrylate family, n-butyl methacrylate is produced by the same process as methyl methacrylate - alcoholysis of methacrylamide with n-butanol. There are two major applications for n-butyl methacrylate - as a modifier in polymers for industrial and automotive lacquers and as a comonomer with higher methacrylates (e.g., lauryl and stearyl) in the manufacture of lubricant viscosity index improvers.

The butyl glycol ethers are also primarily coatings end use oriented. Approximately 22 percent of U.S. n-butanol demand is consumed in the manufacture of ethylene glycol mono-n-butyl ether (butyl CELLOSOLVE®) and diethylene glycol mono-n-butyl ether (butyl CARBITOL®).

The principal application for butyl CELLOSOLVE is as a low evaporating solvent of choice in many industrial coatings applications including coil coating and wood finishing. Its acetic acid ester, butyl CELLOSOLVE acetate, finds use in similar applications as a coalescing aid in latex trade

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paints. As an ingredient in many specialty household products, butyl CELLOSOLVE (and other glycol ethers) has three main functions:

- as an aid in removal of water soluble or water dispersible soils.
- as a coupling agent.
- as a filming or coalescing aid in water-borne floor polishes.

Butyl CARBITOL is used in trade paint formulations and, as in the case of its acetic acid ester, as a coalescing aid. Small amounts of triethylene glycol mono-n-butyl ether are used in hydraulic brake fluid systems. The butyl glycol ethers are increasing in volume at a rate of about 5 percent per year.

Demand for n-butanol as n-butyl acetate accounts for about 13 percent of domestic consumption of the alcohol. This acetate ester is a general purpose coatings solvent with particular application in nitrocellulose lacquers and moisture cured urethane coatings formulations. n-Butyl acetate is the traditional medium boiling solvent for nitrocellulose lacquers and, as such, is the standard by which other solvents are compared.

Manufacture of butylamines (n-butanol and ammonia) accounts for about 2 percent of n-butanol demand. The C_4 amines are used primarily as intermediates in the manufacture of herbicides, rubber chemicals, and pharmaceuticals. Consumption of n-butanol in butylamines is growing at a rate of about 5 percent per year.

Use of n-butanol in the manufacture of a wide range of plasticizers for PVC and/or other coatings resins represents about 8 percent of domestic demand for alcohol. The principal end use products involved include:

dibutyl phthalate
butyl benzyl phthalate
dibutyl maleate (comonomer for internal plasticization)
dibutyl fumarate (comonomer for internal plasticization)
dibutyl sebacate
butyl stearate

Butyl benzyl phthalate (BBP) is by far the largest volume outlet for n-butanol in the plasticizer market. Monsanto is the world's principal supplier of this fast fusing plasticizer for PVC resin. BBP has become a key plasticizer in vinyl flooring compositions as a result of its stain resistance and processability.

Miscellaneous uses for n-butanol including use as an intermediate in the manufacture of lube oil additives and pharmaceuticals account for about 4 percent of U.S. demand.

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Isobutanol. Isobutanol is consumed primarily as a solvent in surface coatings applications, either directly, or as isobutyl acetate. Both the alcohol and its acetic acid ester are substitutes for n-butanol and n-butyl acetate in many coatings uses, but a significant price differential would be required for major replacement to occur. The iso products are, as a rule, faster evaporating and have somewhat poorer solvency relative to their normal counterparts, hence the normals are preferred and command higher prices. Abnormally high usage of isobutanol occurred in the solvents market in 1979 due primarily to a shortage of n-butanol. In all, about 37 percent of domestic isobutanol demand is centered in the coatings solvent market, as the alcohol per se, or as the acetic acid ester.

Diisobutylamine production (isobutanol and ammonia) for use in the manufacture of herbicides is the largest single chemical intermediate market for isobutanol. It represented approximately 32 percent of U.S. demand for the alcohol in 1979. This application is growing at a rate of roughly 3 percent per year.

Isobutanol use in the manufacture of zinc dialkyl dithiophosphates (ZDDP), anti-wear lube oil additives, represented 13 percent of domestic consumption. Other alcohols used in this application include methylamyl alcohol, primary amyl alcohol, n-butanol, 2-ethylhexanol and isooctanol.

The only remaining use of any importance is the manufacture of a number of specialty phthalate plasticizers for PVC and other resin systems. Plasticizers account for about 8 percent of demand and the remaining 10 percent involve a variety of miscellaneous applications.

2-Ethylhexanol. Use of 2-ethylhexanol in the manufacture of PVC plasticizers, most notably DOP (di-2-ethylhexyl phthalate), has historically accounted for over 70 percent of U.S. demand for this alcohol. DOP has been the most widely used general purpose PVC plasticizer for close to half a century and is considered the "workhorse" of the industry. The material is used in a wide variety of PVC resin applications including flooring, wire and cable, packaging and coated fabrics. In the past, DOP has represented the industry cost/performance standard against which all competing plasticizers were measured.

Shutdown of Oxochem's 2-ethylhexanol unit in 1978 eliminated 300 million pounds of capacity overnight. As a result, DOP users began a crash reformulation effort on alternative plasticizers. Linear alcohol and C_9 and C_{10} branched chain alcohol based phthalates as well as butyl benzyl phthalate, for example, were found to be wholly or partially substitutable plasticizers in many DOP applications. New 2-ethylhexanol capacity available starting in 1981 is expected

to stem the decline in DOP demand and, although the product will probably not regain its dominant position in the industry, further growth should track flexible PVC demand of about 3 percent per year.

Other 2-ethylhexanol based plasticizers include di-2-ethylhexyl adipate for vinyl food wrap application, tri-2-ethylhexyl trimellitate, di-2-ethylhexyl azelate, and di-2-ethylhexyl sebacate.

2-Ethylhexyl acrylate manufacture represented about 15 percent of domestic consumption of the alcohol. The acrylate is the longest chain acrylate ester produced by esterification of acrylic acid. The monomer is used in acrylic copolymers for pressure sensitive adhesives, PVC impact modifiers, and as a comonomer with vinyl acetate and vinyl chloride in latexes for paints and textiles. Growth over the next 5 years is estimated at 6 percent per year.

The alcohol also finds use in the manufacture of lube and fuel oil additives and synthetic lubricants (about 6 percent of domestic consumption). The zinc dialkyl dithiophosphate anti-wear additive based on 2-ethylhexanol provides ideal compatability, oil solubility, and high temperature stability in many lube oils for both spark ignition and diesel engines.

In a fuel additive use for 2-ethylhexanol, the alcohol is reacted with nitric acid and the nitrate produced added in low concentrations to diesel fuel to improve ignition quality. Use of such a "cetane improver" allows the refiner greater flexibility in blending distillate into fuel such as aromatics, branched paraffins, and naphthenes. The "cetane improver" also helps meet sudden local increases in demand for diesel fuels by allowing refiners to upgrade stored heating oil to diesel fuel quality quickly and economically.

Diester synthetic base stock lubricants formulated with 2-ethylhexanol (e.g., di-2-ethylhexyl adipate) provide excellent low temperature starting properties in automotive crank case applications and are also employed as lubricants for industrial machinery such as compressors and turbines.

About 4 percent of 2-ethylhexanol domestic demand is consumed in the manufacture of di-2-ethylhexyl sulfosuccinate - a general purpose anionic surfactant used in textile processing.

Miscellaneous uses for 2-ethylhexanol include specialty surfactants, anti-foaming agents, esters of boric and chloroformic acid, and specialty solvents.

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7

Manufacture of Higher Straight-Chain Alcohols by the Ethylene Chain Growth Process

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The first commercial volumes of higher molecular weight, linear alcohols were prepared from naturally occurring fats and oils. Because of this origin, these alcohols, even the synthetic versions, are commonly called "fatty alcohols." Another common name for these products is "detergent-range alcohols," after their highest volume use. This name helps to distinguish alcohols with eleven or more carbons from alcohols with six to ten carbons which are known as "plasticizer alcohols," after their highest volume use.

For this discussion we will arbitrarily define higher molecular weight or detergent-range alcohols as those with eleven or more carbon atoms. As with many boundaries, the one between plasticizer and detergent alcohols is not distinct. Many detergent intermediates contain only ten carbon alcohols and Shell has recently introduced a new product which contains the nine through eleven carbon homologs. On the other hand, isotridecyl alcohol, a C_{13} oxo alcohol, is commonly used as a plasticizer feedstock.

Coconut oil and tallow were the principal raw material sources for early fatty alcohol manufacture. Coconut oil is a lauryl-range oil and affords primarily C_{12} and C_{14} alcohols. Tallow is a stearyl-range oil and yields primarily C_{16} and C_{18} alcohols. Both of these natural products form only even carbon-numbered alcohols. Some synthetic alcohols contain both even and odd carbon-numbered alcohols while other synthetic alcohols are like the natural products and contain only even carbon-numbered homologs.

It was recognized in the late 1950's that the supply and therefore price of naturally occurring products, such as coconut oil and tallow, could fluctuate widely. Both political and climatic conditions have an influence on the supply and price of these oils, and the price of naturally-derived alcohols depends on their raw material costs. With both politics and climates to content with, natural alcohol producers often have little control over the price of their final product.

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This situation provided an incentive for development of synthetic routes to fatty alcohols.

Synthetic fatty alcohols fall into three broad categories and are manufactured from two basic raw materials--ethylene and n-paraffins. One group is secondary alcohols which are prepared by oxidation of n-paraffins in the presence of boric acid. A second group consists of oxo alcohols manufactured by hydroformylation of linear olefins which are derived from either n-paraffins or ethylene. Both of these alcohol types are discussed in separate chapters. The last group is Ziegler alcohols which are prepared from ethylene and are the primary subject of this chapter.

Secondary alcohols are much different chemically than primary alcohols, such as natural alcohols. In addition, commercial secondary alcohols are prepared from both even and odd carbon-numbered n-paraffins and thus contain both even and odd carbon-numbered alcohols. Oxo alcohols are primary alcohols, as are natural alcohols. However, oxo alcohols contain from twenty to sixty percent branched chain alcohols and also contain both even and odd carbon-numbered homologs. Ziegler alcohols are very similar to natural alcohols. They are primary alcohols and are a mixture of only even carbon-numbered homologs. The major differences between Ziegler and natural alcohols are trace impurities present and the range of synthetic products, C_4-C_{30}, available.

Natural Alcohols

As noted earlier, natural alcohols are produced from coconut oil and tallow as well as some other fats and oils--palm kernel oil, palm oil, sperm whale oil, etc. Most of these natural oils actually consist of fatty triglycerides, i.e., glycerol esterified by three molecules of fatty acid. There is very little free alcohol present in these materials, and the alcohols are derived from the fatty acid moiety of the triglyceride by reduction.

Each triglyceride molecule has a random distribution of acid chain lengths and degrees of unsaturation. However, the composition of fats and oils from a common source is relatively uniform. While fatty alcohols theoretically could be derived from any fat or oil, most are prepared from coconut oil or tallow with an increasing quantity derived from palm oil or palm kernel oil. Approximate compositions (1) of these four oils are listed in Table I.

The first commercial production of fatty alcohols in the 1930's employed a sodium reduction process (Bouveault-Blanc) (2). However, the high usage (4 mol/mol alcohol) of expensive sodium soon led to replacement of this method of reduction by catalytic hydrogenation.

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TABLE I

Fatty Acid Composition, Weight Percent

	Coconut Oil	Palm Kernel Oil	Tallow	Palm Oil
C_6	0.8	–	–	–
C_8	5.4	2.7	–	–
C_{10}	8.4	7.0	–	–
C_{12}	45.4	46.9	–	–
C_{14}	18.0	14.1	6.3	1.4
C_{16}	10.9	8.8	27.4	40.1
C_{18}	9.9	20.5	66.2	58.5
C_{20}	0.4	–	–	–

There are basically two types of hydrogenation processes—hydrogenation of methyl esters and hydrogenation of fatty acids—with the former predominating in the U.S. Ashland and Procter & Gamble, the two U.S. fatty alcohol producers, both utilize methyl ester-based processes (3).

In the methyl ester route (Figure 1), refined triglycerides are reacted with methanol in the presence of a sodium methoxide catalyst to form the corresponding fatty acid methyl esters and glycerine (2).

$$C_3H_5(O\overset{O}{\overset{\|}{C}}R)_3 + 3CH_3OH \xrightarrow{NaOMe} 3R\overset{O}{\overset{\|}{C}}OCH_3 + C_3H_5(OH)_3$$

This is a batch reaction carried out at atmospheric pressure with refluxing methanol. The crude reaction mixture is phase-split, and commercial glycerine is recovered from the lower phase by separating excess methanol.

The methyl esters can be fed directly to a hydrogenation unit, or more often are distilled to separate unreacted triglycerides which are recycled. The distilled methyl esters are hydrogenated at approximately 300°C and 3000 psig with a copper chromite catalyst in slurry form through tubular reactors. Excess hydrogen is used for reduction as well as agitation of the slurried catalyst.

$$R\overset{O}{\overset{\|}{C}}OCH_3 + 2H_2 \longrightarrow RCH_2OH + CH_3OH$$

The product mixture is flashed to separate hydrogen and some methanol. Catalyst is then separated from crude alcohol via centrifugation and recycled to the reactor as a slurry.

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The last traces of catalyst are removed from crude alcohol by filtration. Crude alcohol is then stripped at atmospheric pressure to remove methanol and vacuum distilled to isolate the desired alcohol fractions.

Ziegler Alcohols

In the mid 1950's, Dr. Karl Ziegler (4) and his associates at the Max Planck Institute carried out fundamental research which provided the basis for schemes to synthesize even carbon-numbered, linear alcohols similar to natural alcohols. Commercial plants were built by Conoco in 1962, Condea in 1964, and Ethyl in 1965. The Conoco and Condea processes are virtually identical and different from the Ethyl process.

There are four basic parts of a Ziegler alcohol process.

1. Preparation of triethylaluminum.
2. Growth with ethylene to higher alkylaluminum compounds.
3. Oxidation to aluminum alkoxides.
4. Hydrolysis to product alcohols.

Both the Conoco and Ethyl processes use these four basic steps, and Ethyl adds a transalkylation step to control product distribution.

Synthesis of triethylaluminum from aluminum, hydrogen, and ethylene is the first segment of a Ziegler alcohol process. It can be carried out in a single step, but normally is accomplished on a commercial scale in two stages with recycle of two-thirds of the trialkylaluminum product.

$$4Al(C_2H_5)_3 + 2Al + 3H_2 \longrightarrow 6Al(C_2H_5)_2H$$

$$6Al(C_2H_5)_2H + 6CH_2{=}CH_2 \longrightarrow 6Al(C_2H_5)_3$$

$$\overline{2Al + 3H_2 + 6CH_2{=}CH_2 \longrightarrow 2Al(C_2H_5)_3}$$

Hydroaluminum of triethylaluminum forms diethylaluminum hydride. A Conoco patent (5) indicates the hydrogenation reaction is catalyzed by titanium and zirconium in the feed aluminum and probably does not occur with ultrapure aluminum. Ethylene readily adds to the resulting diethylaluminum hydride to yield triethylaluminum.

In the chain growth step, ethylene adds to triethylaluminum to form higher trialkylaluminum compounds with an even number of carbon atoms.

$$Al(C_2H_5)_3 + mCH_2{=}CH_2 \longrightarrow Al[(CH_2CH_2)_mCH_2CH_3]_3$$

The mole percent distribution of alkyl chains follows a Poisson curve (6,6a). The average number of ethylene units added during this growth step is commonly referred to as the "m-value" and

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is a good description of the distribution of alkyl groups on aluminum.

Addition of ethylene to triethylaluminum is first-order in monomeric triethylaluminum and ethylene (7). Since triethylaluminum is largely dimeric in the liquid phase, kinetics of the growth reaction take the following form:

$$[Al(C_2H_5)_3]_2 \rightleftarrows 2Al(C_2H_5)_3 \xrightarrow{C_2H_4} 2AlR_3$$

$$-\frac{d[C_2H_4]}{dt} = k[Al(C_2H_5)_3]^{\frac{1}{2}}[C_2H_4]$$

There are three side reactions which occur during the growth step (8). At higher temperatures (>120°C), aluminum alkyls crack to form dialkylaluminum hydride and α-olefins (thermal displacement).

$$(RCH_2CH_2)_3Al \rightleftarrows (RCH_2CH_2)_2AlH + RCH{=}CH_2$$

Because of the large excess of ethylene present in the growth reactor, the reverse reaction is insignificant. Ethylene reacts with dialkyl aluminum hydride much more rapidly than does the terminal olefin, and any alkyl group thermally displaced is replaced by an ethyl group. However, terminal olefin present in the growth reactor can react with trialkylaluminum compounds. The α-olefin inserts between the aluminum-carbon bond just as ethylene does in a normal growth process.

$$R_3Al + RCH{=}CH_2 \rightleftarrows R_2AlCH_2\text{-}\underset{\displaystyle R}{\underset{|}{C}H}\text{-}R$$

This side reaction leads to the formation of branched alcohols as well as branched olefins. These impurities are dimeric and are about twice the average molecular weight as the product alcohols.

The third side reaction is formation of a small amount of polyethylene during the growth step. The quantity of polyethylene does not represent a significant yield loss, but does present serious processing problems. The polymer deposits on reactor surfaces, inhibits heat transfer, plugs valves, and must be cleaned out periodically. A Conoco patent (9) indicates this problem can be prevented by addition of small quantities of carbon monoxide to the feed ethylene.

The next step in a Ziegler process is oxidation of the trialkylaluminum growth mixture to the corresponding aluminum alkoxides.

$$2R_3Al + 3O_2 \longrightarrow 2(RO)_3Al$$

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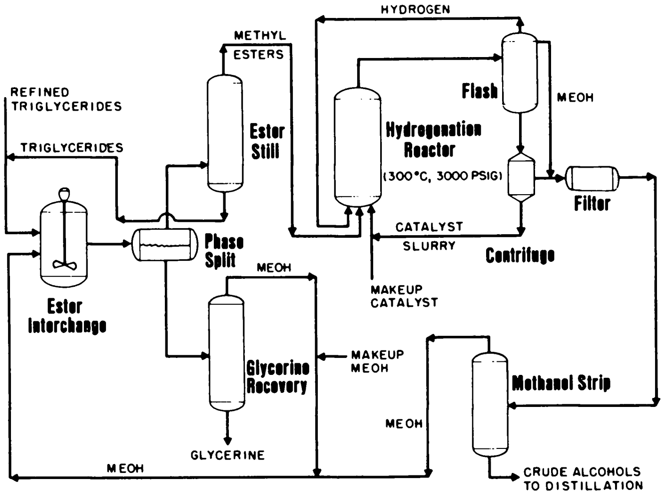

Figure 1. Methyl ester hydrogenation

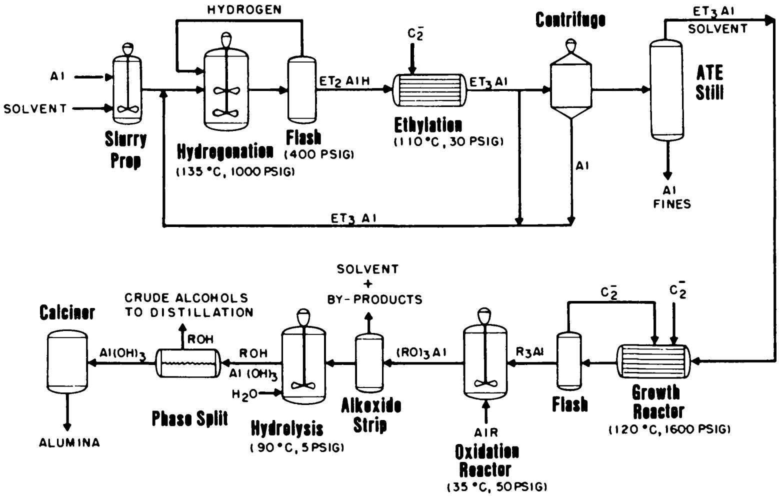

Figure 2. ALFOL alcohol process

This step is carried out very carefully using dry air. The reaction is rapid and exothermic. By-products of the oxidation include aldehydes, esters, paraffins, and free alcohols.

The final step is hydrolysis of aluminum alkoxides to free the product alcohols.

$$(RO)_3Al + 3H_2O \longrightarrow 3ROH + Al(OH)_3$$

Hydrolysis can be carried out with water, as shown above, in which case the co-product is aluminum hydroxide. This aluminum hydroxide is converted to alumina by drying and calcining (10).

Aluminum alkoxides can also be hydrolyzed with dilute sulfuric acid in which case the co-product is aluminum sulfate.

$$2(RO)_3Al + 3H_2SO_4 \longrightarrow 6ROH + Al_2(SO_4)_3$$

Aluminum sulfate is a salable co-product in conventional markets, but it is of low value.

Conoco ALFOL Alcohol Process (11)

The ALFOL alcohol process is described in Figure 2. Conoco uses a two-step process for the synthesis of triethylaluminum--hydrogenation followed by ethylation. Triethylaluminum in a solvent and hydrogen are circulated through a hydrogenation reactor. Slurried aluminum powder is added and reacts with the triethylaluminum and hydrogen to form diethylaluminum hydride. The hydrogenation reaction is carried out at 135°C and 1000 psig in an agitated vessel with an average residence time of one hour.

Powdered aluminum containing the patented (5) activators is available in railcar quantities. This powder is slurried with a dry solvent. Conoco uses a highly paraffinic solvent to ensure that product alcohols will meet FDA standards.

Effluent from the hydrogenation reactor is depressured to about 400 psig. This level of hydrogen is required to prevent the reverse reaction, diethylaluminum hydride decomposition, which results in plating of aluminum on the process equipment. Product diethylaluminum hydride, unreacted aluminum, and solvent are charged to the ethylation reactor. Ethylene is introduced and undergoes a rapid, exothermic reaction to form triethylaluminum. A tubular reactor with high heat transfer capabilities is required to control this reaction (12).

The triethylaluminum reaction product is divided into two streams. One stream, 70-75 percent of the total, is recycled directly to the hydrogenation unit to form additional diethylaluminum hydride. The other stream, 25-30 percent of the total, is the actual product stream. It is first centrifuged to remove the bulk of unreacted aluminum which is recycled to the hydrogenation reactor along with recycle triethylaluminum. Product

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triethylaluminum and solvent are then distilled from unreacted aluminum fines to produce high purity triethylaluminum.

The next step in the ALFOL alcohol process is chain growth. Triethylaluminum is preheated to 115°C in the first tubes of the growth reactor before ethylene is added. Ethylene is injected at several points along the length of the reactor to provide make-up ethylene as well as to help control the reaction temperature. Temperature control of this highly exothermic growth reaction is difficult and a special reactor design has been perfected to obtain good heat transfer.

The growth reaction is carried out below 130°C to prevent the alkyl decomposition or thermal displacement (13) described earlier. Ethylene pressure is maintained at approximately 1600 psig. Temperature, pressure, and residence time are adjusted to obtain the desired extent of chain growth or "m-value." Excess ethylene is flashed from the trialkylaluminum product or "growth product" and recycled.

Oxidation of the trialkylaluminum mixture is carried out using dry air in agitated batch reactors in the ALFOL alcohol process. Reactor temperature is maintained at approximately 35°C by cooling and the oxidation is operated at about 50 psig. Approximately six hours is required for each batch of growth product to be completely oxidized. The oxidation reactors are operated in staggered fashion to minimize the maximum heat load.

The aluminum alkoxide mixture or "oxidized growth product" is fed to a series of vacuum flash evaporators to remove solvent introduced earlier in the triethylaluminum preparation. This vacuum stripping step also removes olefins formed during the growth reaction and the myriad of by-products formed during oxidation (14). Efficiency of this stripping process is a key factor in alcohol product quality. This is the opportunity to separate volatile impurities--olefins, esters, aldehydes, paraffins, etc.--from product alcohols while the alcohols are in a nonvolatile form (aluminum alkoxides).

Stripped alkoxides are then sent to the hydrolysis reactor. In the current ALFOL alcohol process, hydrolysis is accomplished using water instead of dilute sulfuric acid which results in a mixture of alcohols and alumina slurry being formed in the hydrolysis reactor. This mixture is phase separated.

Alcohols are dried and sent to a distillation train where they are separated by conventional fractional distillation. Crude alcohols are separated into C_2-C_4, C_6-C_{10}, C_{12}-C_{14}, C_{16}-C_{18}, and C_{20}+ fractions. High purity, individual homologs are prepared by redistillation of the appropriate mixture. The product alcohols are marketed as ALFOL alcohols by Conoco Chemicals.

The alumina slurry is dried and then calcined to form a very active, high purity alumina which is marketed by Conoco Chemicals as CATAPAL alumina. Because of this unique process of manufacturing the alumina, it has a very low sodium content

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and almost no other trace metals are present. The alumina is in high demand as a catalyst support since it is nearly free of contaminants which can alter the performance of a catalyst. A catalyst manufacturer can attach only the metals he wishes to attach and be assured of their effects.

Ethyl Modified Linear Alcohol Process (15)

Ethyl's version of the Ziegler alcohol process has been modified in order to control the product alcohol distribution. Whereas the Conoco ALFOL alcohol process affords the full range of alcohols, C_2-C_{30}, in a Poisson distribution, Ethyl's product distribution can be modified, for example, as shown in Figure 3 to give carbon number distributions to fit the needs of the market.

Table II

Typical Homolog Distributions

Carbon Homolog	Conoco ALFOL Process	Ethyl EPAL Process
2	0.5	Trace
4	3.4	0.1
6	9.5	1.5
8	16.1	3.5
10	19.5	8.0
12	18.4	34.0
14	14.1	26.0
16	9.1	16.0
18	5.1	8.8
20	2.5	1.9
22	1.1	0.2

The following discussion is based on an interpretation of patent literature. The Ethyl process consists of five basic steps instead of four.

1. Preparation of triethylaluminum.
2. Growth of ethylene to higher alkylaluminum compounds.
3. Transalkylation and separation of trialkylaluminum compounds.
4. Oxidation of aluminum alkoxides.
5. Hydrolysis to product alcohol.

Since the Conoco ALFOL alcohol process has already been described in detail, only those areas where the two processes are different will be covered. Preparation of triethylaluminum appears similar in both processes. Ethyl's scheme is believed to use a ballmilling procedure to obtain an active aluminum

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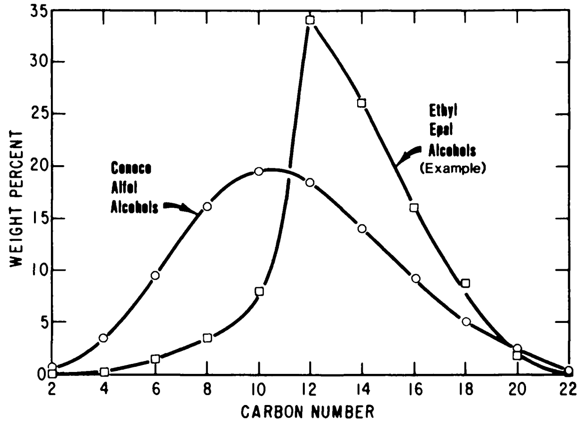

Figure 3. Alcohol distribution

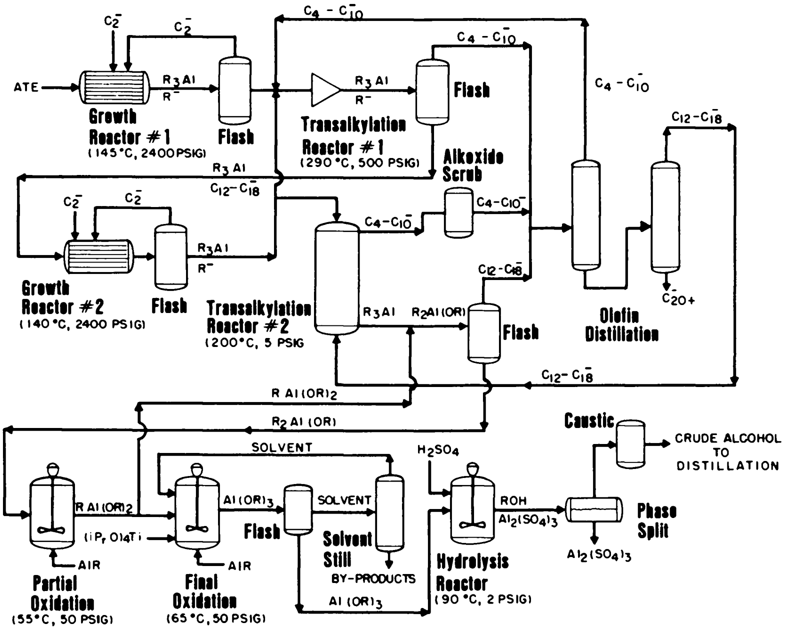

Figure 4. Ethyl process (based on patent literature)

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powder but the chemistry is identical. The Ethyl process, after triethylaluminum preparation, is shown in Figure 4. Ethyl patents (16) indicate two growth reactors, two transalkylation reactors, and two olefin stills are used to accomplish the desired alcohol peaking process.

In the first growth reactor, triethylaluminum is grown with ethylene as in the ALFOL alcohol process. However, the Ethyl growth process is extended to a lower "m-value" (3 vs. 4) and is carried out at higher temperature (130°-150°C) and pressure (2000-2500 psig). Exact reaction conditions will be determined by the "m-value" or alcohol distributin desired as well as the relative quantity of trialkylaluminum and olefins one wishes to produce (17). The higher growth temperature used in the Ethyl process will produce a significant quantity of lower molecular weight α-olefins via thermal displacement. These olefins are used to alter the product distribution of the aluminum alkyls and thus the alcohols. After growth, excess ethylene is removed in a flash drum and recycled.

The first growth product and its contained low molecular weight α-olefins are reacted with a large excess of α-olefins (C_4-C_{10}) in a transalkylation reactor. This reactor is a venturi-type reactor (18) operating at 275°-300°C, 500 psig, and a short residence time of about 0.5 seconds. Heat is supplied to the reactor by super heating the large α-olefin stream. Immediate quenching of this product to about 120°C is required to suppress undesirable side reactions, such as dimerization and isomerization of the α-olefins.

The trialkylaluminum compounds leaving this transalkylation reactor now contain primarily C_4-C_{10} alkyl groups simply by the law of mass action. The low molecular weight olefins are separated from the trialkylaluminum compounds by distillation (19). This is a specially designed flash unit which contains provisions for scrubbing the overhead olefin vapors with partially (2/3) oxidized alkylaluminum dialkoxide to remove any trialkylaluminum carried overhead (20).

$$RAl(OR)_2 + R_3Al \longrightarrow 2R_2Al(OR)$$

Scrubbing provisions of this unit are not shown in Figure 4 for simplicity. Low molecular weight α-olefins are sent to olefin fractionation, and the low molecular weight trialkylaluminum compounds and high molecular weight olefins are sent to a second growth reactor.

Reaction conditions in the second growth reactor are similar to those in the first. Only a limited amount of chain growth occurs in this reactor such that the C_4-C_{10} trialkylaluminum compounds are grown to about C_8-C_{14} trialkylaluminum compounds. Again excess ethylene is removed in a flash drum and recycled.

This second growth product is fed to a second transalkyl-

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ation reactor along with a $C_{12}-C_{18}$ α-olefin stream. Again, an Ethyl patent (21) indicates this is a countercurrent reactor in which the trialkylaluminum compounds are contacted with vapor phase α-olefins. The countercurrent design of this reactor permits the use of only a slight excess of detergent-range $C_{12}-C_{18}$ α-olefins instead of the large excess required by the cocurrent, venturi-type reactor. Reaction conditions are about 200 C and near atmospheric pressure (2-5 psig). Products exiting this reactor are trialkylaluminum compounds with primarily $C_{12}-C_{18}$ alkyl groups and a full range of α-olefins, C_4-C_{30}.

A slip-stream (1/5 to 1/3) of the second growth product can be sent to the first transalkylation reactor rather than the second. This procedure is required in order to balance this growth scheme.

Vapor-phase olefins from the second transalkylation reactor are scrubbed as before with alkylaluminum dialkoxide to remove any trialkylaluminum compounds and then sent to olefin distillation. Detergent-range trialkylaluminum compounds and high molecular weight olefins are blended with sufficient partially (2/3) oxidized growth product to convert the entire mixture to a blend having at least one alkoxide group per aluminum atom. This reaction is rapid and does not require a separate vessel, but can take place in the transfer lines. Conversion to monoalkoxide renders the aluminum compounds less volatile. High molecular weight olefins are then separated from the partially (1/3) oxidized growth product via a special flash unit similar to the one described earlier (20) and sent to olefin distillation.

The partially (1/3) oxidized growth product is sent to an oxidation unit where it is oxidized with dry air to an average of two alkoxide groups per aluminum atom (2/3 oxidized).

$$R_2Al(OR) + O_2 \longrightarrow RAl(OR)_2$$

This partial oxidation reactor is believed to operate at about 55°C. The partially (2/3) oxidized material is used as feed for the three scrubbers described above and for exchanging with unoxidized growth product to form a 1/3 oxidized product. The major use for the 2/3 oxidized growth product is as feed to the final oxidation reactor.

The final oxidation is a batch process as in the ALFOL alcohol process. A hydrocarbon solvent for viscosity control must be added prior to oxidation since none was introduced earlier. Based on patent literature (22), oxidation with dry air takes place in an agitated reactor at approximately 65° C and 50 psig in the presence of a titanium promoter which improves the oxidation selectivity.

The product aluminum trialkoxides are then stripped in a flash evaporator to remove solvent and oxidation by-products described earlier. The light hydrocarbon solvent is separated

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from these by-products via distillation and recycled to the oxidation reactor.

The aluminum trialkoxides are then hydrolyzed with dilute sulfuric acid in the Ethyl process (23). This forms free alcohol and an aqueous aluminum sulfate solution which are separated by phase split. The aqueous aluminum sulfate is sold. Product alcohols are washed with caustic to remove traces of acid, dried, and fed to conventional distillation train. The product alcohols are sold by Ethyl under the trade name of EPAL alcohols.

The Ethyl EPAL process is more complex than the Conoco ALFOL alcohol process. This complexity permits the flexibility of producing both α-olefins and alcohols from the same processing unit as well as having considerable control over the product homolog distributions. Penalties paid for this flexibility are increased capital cost for a more complex process and production of some branched alcohols.

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8

Applications of Higher Alcohols in Household Surfactants

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The major derivatives of normal primary higher alcohols used in the detergent industry include:

1. Alcohol ethoxylates (nonionics).
2. Alcohol ether sulfates.
3. Alkyl sulfates.
4. Miscellaneous--Including two other comparatively minor products--amine oxides and alkyl glyceryl ether sulfonates.

Smith(1) gives an excellent review of commercial surfactants and others have reviewed the formulation of household products(2).

Chemistry

Nonionics. The alcohol nonionics are processed according to the following:

$$ROH + n\ CH_2\overset{O}{-}CH_2 \longrightarrow RO(CH_2\text{-}CH_2O)_nH$$

The amount of ethylene oxide will generally be at least 60 percent of the total weight of the finished ethoxylate to give the best properties. This would be about 7 moles on a lauryl (C_{12}) range alcohol and 9 to 10 moles of ethylene oxide on a stearyl (C_{18}) range alcohol.

These resulting nonionics can be used in heavy-duty powders, heavy-duty liquids, and hard-surface cleaners.

Alcohol Ether Sulfates. The ether sulfates are prepared by the sulfation of alcohol ethoxylates as shown in the steps below:

$$RO(CH_2\text{-}CH_2O)_3H \xrightarrow[\text{2. NaOH}]{\text{1. } SO_3} RO(CH_2\text{-}CH_2O)_3SO_3Na + H_2O$$

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The starting ethoxylate is generally the 3-mole adduct but can be as low as a 1-mole ethoxylate. Sulfating agents can be SO_3, chlorosulfonic acid, or sulfamic acid. A variety of neutralizing agents can be used--including NaOH, ammonia, triethanolamine, and $Mg(OH)_2$.

The ether sulfates are used in light-duty liquids, heavy-duty powders, and shampoos.

<u>Alkyl Sulfates</u>. The alkyl sulfates or alcohol sulfates are prepared very similarly to the ether sulfates shown above.

$$ROH \xrightarrow[2.\ NaOH]{1.\ SO_3} ROSO_3Na + H_2O$$

The alcohol sulfates are used in heavy-duty powders and shampoos.

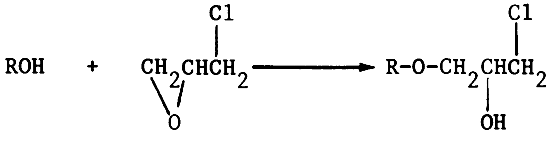
<u>Miscellaneous</u>. The amine oxides used in household products are generally alkyl dimethyl amine oxides and are prepared from alcohols as shown below:

$$ROH \xrightarrow[2.\ (CH_3)NH]{1.\ HCl} RN(CH_3)_2$$

$$RN(CH_3)_2 + H_2O_2 \longrightarrow R\overset{CH_3}{\underset{CH_3}{N}} \rightarrow O$$

These alkyl dimethyl amine oxides are used as foam stabilizers primarily in light-duty liquids and shampoos where the major active ingredient is either an alcohol ether sulfate or an alcohol sulfate. The alkyl group is usually C_{12} to C_{14} which gives the best overall foam stability(3).

The alkyl glyceryl ether sulfonates are prepared as follows:



Linear Alcohol　　Epichlorohydrin　　Alkyl Ether Chlorohydrin

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In Monohydric Alcohols; Wickson, E.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1981.

$$R\text{-}O\text{-}CH_2\underset{\substack{|\\ OH}}{\overset{\substack{Cl\\ |}}{C}}HCH_2 + Na_2SO_3 \longrightarrow R\text{-}O\text{-}CH_2\underset{\substack{|\\ OH}}{\overset{\substack{SO_3Na\\ |}}{C}}HCH_2$$

Alkyl Ether Chlorohydrin	Sodium Sulfite	Alkyl Glyceryl Ether Sulfonate

These products can be found in light-duty liquids and in some shampoos and detergent bars and are primarily used to enhance skin emolliency and "cleaning ability."

Nonionics

Heavy-Duty Powders. Nonionics find use in the major volume household product, heavy-duty powders. The words heavy duty are synonymous with laundry applications. Products of this type follow the general formulation as shown below:

10 percent nonionic.

25 to 35 percent sodium tripolyphosphate (or sodium carbonate).

5 to 10 percent meta-silicate.

q.s. sodium sulfate and other minor constituent additives (bleach, perfume, antiredeposition agents, color, etc.).

The optimum alcohol and amount of ethylene oxide is dependent upon the type of soil and the type of foam desired for for the finished product. Figure 1(4) shows the optimum ethylene oxide content in a heavy-duty powder formulation similar to that shown in the foregoing. Lines are "isodets"--lines of equal detergency ranging from a lower detergency rating of 1 to a high of 4.

Figure 1 shows that the optimum detergency is exhibited in the 62 percent ethylene oxide range. On an alcohol of C_{12} to C_{14}, this would amount to about 7 moles of ethylene oxide. A higher alcohol molecular weight could result in an ethylene oxide content approaching 10 moles. This detergency was that exhibited on a combination of three types of standard soiled cloths.

The optimum alcohol ethoxylate on oily soils can be different. Nonionics have the advantage of performing exceptionally well in comparison to other types of active ingredients with oily soils. The choice of product can

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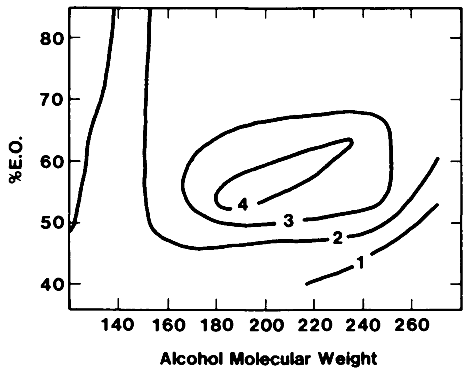

Figure 1. Heavy-duty detergency alcohol, nonionic (0.2% concentration; 50 ppm hardness; 120°F)

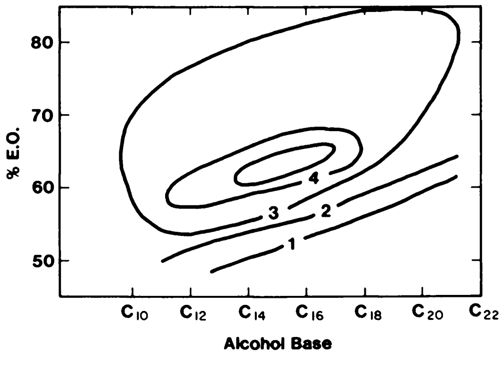

Figure 2. Heavy-duty detergency nonionic isodets (0.4% concentration; 300 ppm hardness; 190°F)

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also depend upon the temperature of use(5) as well as the type of foam desired.

Figure 2 shows isodets at high temperature, high hardness, and high concentration giving a different optimum than at the lower conditions of Figure 1. Foam and detergency profiles on different soil types with different wash temperatures can be found in the literature(4-10).

Heavy-Duty Liquids. Heavy-duty laundry liquids have gained much importance and much interest in the literature over the last few years. Products in the industry today include both built and nonbuilt heavy-duty liquids. Built heavy-duty liquids are those which contain a builder such as tetrapotassium pyrophosphate (TKPP) or sodium citrate in order to sequester calcium and magnesium hardness ions. Nonbuilt heavy-duty liquids contain no builders and make up for that shortage by considerably increased active contents in order to maintain performance(8-14). Built heavy-duty liquids can have either of the following types of formulations:

10% Nonionic	10% Alkylbenzene sulfonate
10-20% TKPP or citrate	0-15% Nonionic
5-10% Hydrotrope	10-20% TKPP or citrate
q.s. H_2O	5-10% Hydrotrope
	q.s. H_2O

Nonbuilt heavy-duty liquids can contain either a high ratio of nonionic to linear alkylbenzene sulfonate (LAS) or, more recently, a reverse type ratio. Typical formulations of these types of products are given below:

30-35% Nonionic	or	25-35% LAS
10% LAS		10-15% Nonionic
5-10% Solubilizer		5-10% Solubilizer
45-55% H_2O		40-60% H_2O

Again, the optimum nonionic of choice for this application will depend upon the type of soil to be removed in the laundry process. For example, Figure 3 shows the optimum nonionic for removing typical sebum soil (body oil) in a nonbuilt heavy duty liquid. This figure shows that the optimum lies in the circle between C_{12} and C_{16} alcohol at an ethylene oxide level of 60 to 80 percent. The peak of this optimum would be in the vicinity of a C_{14} alcohol with 70 percent EO. This is considerably higher in EO content than the ethylene oxide optimum found for powdered laundry detergents.

At the same time, as previously mentioned, different types of soil can give different optimums. For example,

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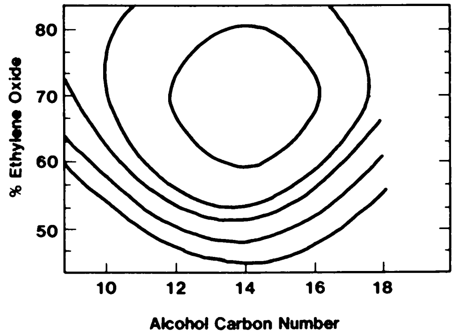

Figure 3. Formulation 50% nonionic q.s. water (test conditions: 120°F; 150 ppm; 0.10% sebum soil)

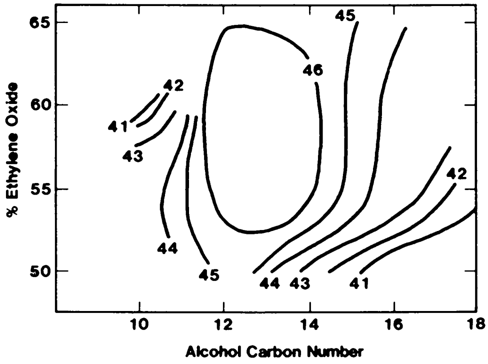

Figure 4. Motor oil (300 ppm)

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in Figure 4, we find that with motor oil soil, the optimum detergency(46) is considerably narrower and is about a C_{13} alcohol with 60 percent ethylene oxide.

Most manufacturers are very interested in utilizing optimum performances to make advertising claims and, therefore, will evaluate a large number of soils. The choice of high nonionic/alkylbenzene sulfonate ratio as compared to a reverse high alkylbenzene sulfonate/nonionic ratio again depends upon the choice of foaming ability and the choice of soils to be removed.

The high nonionic formulation gives better performance with sebum soils, whereas excellent performance on certain oily soils can be obtained through the use of alkylbenzene sulfonates at the high sulfonate to nonionic ratio.

General-Purpose Cleaners. These are products which can be used for a variety of household applications including spray or bucket cleaners to be used to wash walls, woodwork, porcelain, linoleum, etc. These products generally contain much smaller amounts of active, as they are to be used in a more concentrated form for eventual dilution with water in actual application. These products can contain 5 to 10 percent nonionic in the total liquid and may also contain TKPP as well as certain solvents such as ethylene glycol mono n-butyl ether. The general choice of products for this application would be the standard C_{12} to C_{13} alcohols with 60 to 70 percent ethylene oxide. However, a C_{10} alcohol ethoxylate offers excellent grease cutting and hard surface cleaning properties.

Ether Sulfates

Heavy-Duty Powders. Although the number of products in which one finds alcohol ether sulfates in laundry products is exceptionally small, the volume is fairly high due to the volume of those specific products. The ether sulfate which is generally used in laundry powders is based on a C_{13} to C_{15} average alcohol with 1 to 3 moles of ethylene oxide on the average. Figure 5 shows this to be the highest detergency. Due to the need for spray-drying, these will always be the sodium alcohol ether sulfate. The ether sulfate is normally found in these formulations at a 4 to 5 percent level and is used in conjunction with alkylbenzene sulfonate and/or alcohol sulfates in the formulation. The specific use in this type of product was discussed at the AOCS World Conference(2).

Light-Duty Liquids. Light-duty liquids refer to the liquid products sold today primarily for the end application of dishwashing. They can also be used for the washing

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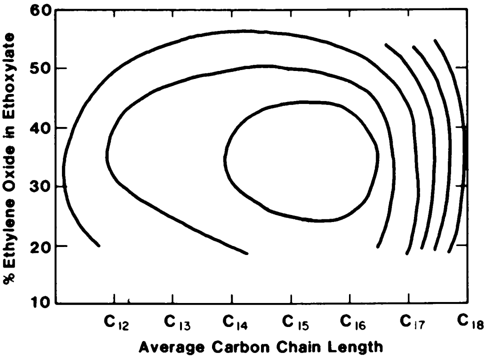

Figure 5. Ether sulfate detergency (0.12%; 150 ppm; 110°F)

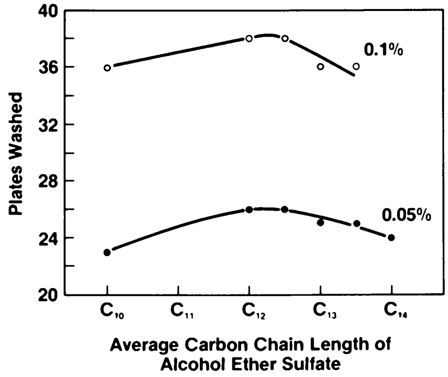

Figure 6. Optimum ether sulfate for ABS/ES light-duty liquids (24/6 LAS/AES—50 ppm hardness)

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of fine fabrics. Light-duty liquids generally fall into two major categories. One of these includes the alcohol ether sulfate as the total major active ingredient. In the other type of formulation, one finds alkylbenzene sulfonate (LAS) and ether sulfate. LAS and ether sulfates work in conjunction with one another to develop a synergistic effect upon foam stability and, as a result, are widely found in the commercial liquid formulations today. The typical ether sulfate product used in either of these types of liquids is a lauryl-range alcohol with about a 3-mole ethylene oxide content (some products may have a mixture of alcohol sulfate and ether sulfate, but in general the overall average EO content is still in the 2- to 3-mole range). Figure 6 shows the optimum carbon chain length for an ether sulfate and substantiates the use today of the C_{12} to C_{13} range. Going above that level, one does not have too much drop off in performance, but this would result in considerably less solubility of the total formulation. Going below the C_{12} optimum will cause a drop in foam stability performance(15).

The following table shows the effect of ethylene oxide upon the solubility of the formulation. From these results, it can be readily understood why the 40 percent ethoxylate (3 mole) is usually used for this application.

EFFECT OF EO CONTENT ON SOLUBILITY OF LD LAS/ES LIQUIDS

ES Portion of Active	Percent EO	Cloud Point (^{o}F)
C_{12}-C_{14}	17.1	48
C_{12}-C_{14}	33.5	34
C_{12}-C_{14}	39.8	30

The optimum ratio of LAS to ether sulfate for foam stability alone is generally in the range of 4:1 LAS/ether sulfate. This can be seen in Figure 7 where the average number of plates washed is plotted against different LAS/ES ratios.

Shampoos. Ether sulfates are extensively used in shampoo formulations in the range of 15 to 25 percent active. The general product of choice is the lauryl-range alcohol with 1 to 3 moles of ethylene oxide. In shampoos, either sodium, ammonium, or triethanolamine salts of the ether sulfate can be used. The choice of these products will be primarily related to the solubility and the finished form of the shampoo. Triethanolamine salts are considerably more soluble and, thus, will be found in a large number

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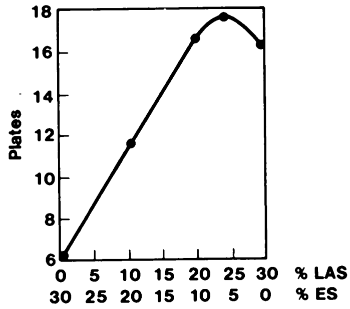

Figure 7. Foam stability—LAS/ES (0.05% concentration; 50 ppm hardness; 115°F, 46°C)

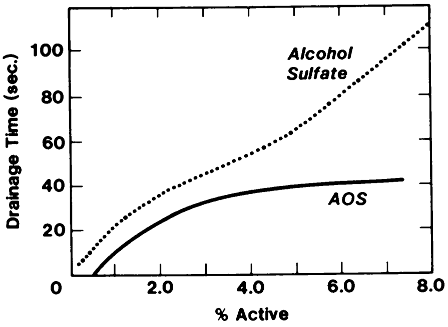

Figure 8. Drainage time at 50 ppm hardness sodium alcohol sulfate vs. AOS

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of liquid products (especially clear liquids). As one moves towards a lotion, cream, or even paste shampoo, products move towards the sodium salt. These shampoos will generally include foam stabilizers to further enhance the foam capacity. These foam stabilizers are normally alkanolamides or amine oxides. The use of the ether sulfate along with these foam stabilizers gives thick copious foam, and this foam is the general property desired for shampoos. There has been over the last few years considerable use of ether sulfates made from 1 to 1 1/2 moles of ethylene oxide on the alcohol. The philosophy behind this use is that one can obtain the thicker, more copious foam of an alcohol sulfate with lesser EO on the alcohol and yet still maintain considerable solubility (more like the ether sulfate).

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Alcohol Sulfates

A major application for alcohol sulfates is its use in conjunction with other active ingredients in heavy-duty laundry powders. In these products, as mentioned before under ether sulfates, one will usually find LAS as well as ether sulfates. Ten to fifteen years ago, a considerable amount of alcohol sulfate was used in conjunction with LAS. These products had a very high content of sodium tripolyphosphate which sequestered the hardness and, as a result, allowed the alcohol sulfate to do its exceptional job of detergency(16). As phosphate contents have been limited, the use of the alcohol sulfate has been reduced due to its sensitivity to harder waters. Another factor which has somewhat slowed down the use of alcohol sulfates is the gradual lowering of wash temperatures from an average of 140°F many years ago (and even boiling temperatures before that time) down to an average of 100°F or less today.

The alcohol sulfate of choice today ranges between a carbon chain average of C_{13} to C_{17}. This alcohol sulfate can be found in some laundry products at 3 to 5 percent of the total formulation.

Shampoos. Like ether sulfates, alcohol sulfates used in shampoos are generally in the range of C_{12} to C_{14} (the lauryl alcohol range). The alcohol sulfate gives an exceptionally thick foam and gives that foam over a wide range of soil concentrations. The alcohol sulfates are the choice product over olefin sulfonates due to the exceptional foamability at the actual higher use concentrations found in washing the hair at high-soil loads (Figure 8). Figure 8 shows this foam stability advantage as a function of film drainage at different shampoo concentrations.

Miscellaneous

As mentioned earlier, the amine oxides are used in dishwashing liquids and in shampoos where the major surfactant is either an alcohol ether sulfate or an alcohol sulfate.

Alkyl glyceryl ether sulfonates are found in some dishwashing liquids, shampoos, and detergent bars and are primarily used to enhance skin emolliency though some claims are made for "cleaning ability."

Abstract

The major derivatives of normal primary higher alcohols used in the detergent industry were discussed. These included alcohol ethoxylates, alcohol ether sulfates, and alkyl sulfates. The chemical reactions for preparation of each were also given.

The applications of each of these derivatives were discussed with typical formulations and optimum carbon chain lengths presented. Usage of alcohol derivatives in laundry products, dishwashing liquids, and shampoos were highlighted.

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9

Secondary Alcohol Ethoxylates

Physical Properties and Applications

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Only a few companies in the world have produced surfactant range higher secondary alcohols until now. The first secondary alcohol plant appeared in the U.S.S.R. in 1959 and has been in operation since then. It has a capacity of about 10,000 tons per year of alcohols having carbon numbers ranging from 13 to 17. The alcohols are mainly used to produce sulfosuccinate esters through esterification with maleic anhydride followed by addition of sodium sulfite. The sulfosuccinate esters are used as raw materials for powder detergents there. Meanwhile, in 1964 in the U.S.A., Union Carbide Corporation commercialized a series of ethoxylated nonionic surfactants based on their secondary alcohols having carbon numbers ranging from 11 to 15 under the registered trade name of TERGITOL 15-S. The plant is believed to have a capacity of 36,000 tons per year of 3 mole ethoxylate of the alcohols. The third plant for higher secondary alcohols was constructed by Nippon Shokubai in Japan in 1972. The plant capacity, originally 12,000 tons per year of 3 mole ethoxylate, was expanded to 18,000 tons per year in 1977 and now is being further expanded to 30,000 tons per year. Nippon Shokubai's products are also sold mainly in the form of ethoxylate under the registered trade name of SOFTANOL. The alkyl carbon range of SOFTANOL is from 12 to 14 so far.

All industries, especially the surfactant and detergent industries, have been heavily involved in various recent controversies such as health and safety problems, resource and energy conservation movements and so on. Under these circumstances, more emphasis has to be placed on key words: SAFETY, RESOURCE SAVING and EFFICIENCY. Only by satisfying these three will there be the chance of developing new technologies and new products.

It is hoped that this presentation will give some ideas for more beneficial use of the products derived from higher secondary alcohols to those who are seeking new technical development in the surfactant and detergent industries.

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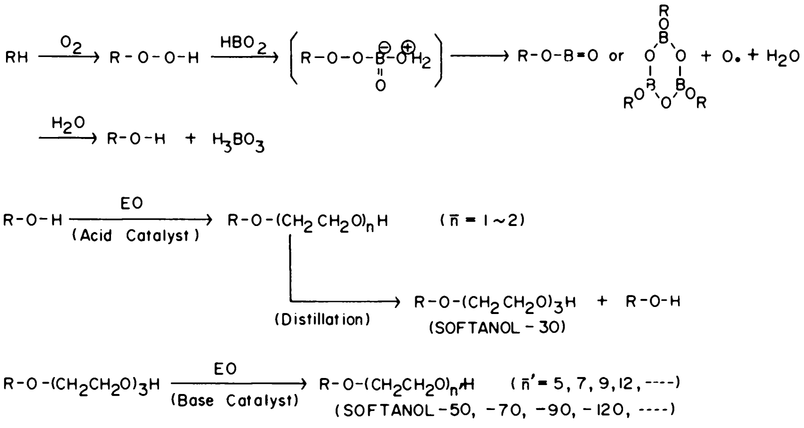

Figure 1. Synthesis route to secondary alcohol ethoxylates from n-*paraffins*

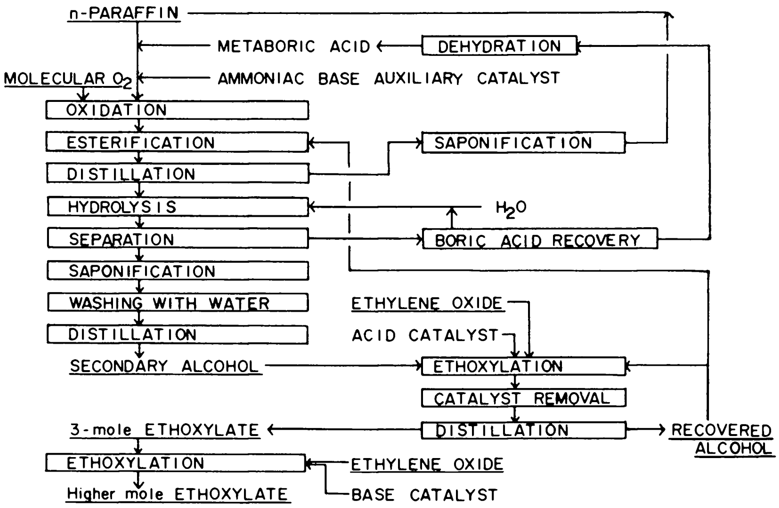

Figure 2. Simplified Nippon Shokubai's process route for secondary alcohols and their ethoxylates

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Manufacturing Process of Secondary Alcohols and Their Ethoxylates

Since previous papers(1,2) describe details of the manufacturing process for secondary alcohols(SA) and their ethoxylates (SAE), only the outline of the process will be presented here. A mixture of secondary alcohols is obtained by liquid phase air-oxidation of normal paraffins in the presence of a boric acid catalyst(Figure 1). Although the existing commercial processes, as developed independently, comprise significantly different combinations of various unit processes, they are all based on this boric acid-modified oxidation of hydrocarbons(3).

In Nippon Shokubai's process(Figure 2), the 3 mole ethoxylate of a mixture of secondary alcohols can be produced from a mixture of normal paraffins through a fully integrated continuous process. The oxidation is carried out using β-metaboric acid as a catalyst and an ammoniac base as an auxiliary catalyst to promote the reaction(4). The alcohol mixture obtained consists of all possible structural isomers of secondary alcohols having the same carbon numbers as the raw material used.

The ethoxylation of secondary alcohols must be first carried out using an acid catalyst to a low degree of polymerization (2). The product, 3 mole ethoxylate, is separated from the reaction mixture by stripping the unreacted alcohol. Further ethoxylation can then be carried out just as with the primary alcohol or alkylphenol using a base catalyst in the conventional manner.

In this process for 3 mole ethoxylate, a mixture of n-paraffins having three successive carbon numbers can be used. The spread of four or more successive carbon numbers may cause difficulties in the separation and purification steps.

Table I shows up-to-date process economics for C_{12-14} secondary alcohols and their 3 mole ethoxylate.

Considerations of Carbon Number Ranges

n-Paraffins are usually isolated from kerosene and have carbon numbers ranging from 10 to 16. As a raw material for Nippon Shokubai's SOFTANOL, C_{12-14} was chosen from the viewpoints of feed stock availability and versatile performance of the products.

Table II shows a typical example of carbon number distribution of n-paraffins in kerosene now available in Japan. To utilize all n-paraffins in kerosene in the near future, it is convenient to divide them, for instance, into three fractions each having three successive carbon numbers, i.e. C_{10-12}(ave. 11), C_{12-14} (ave. 13), and C_{14-16}(ave. 15).

Because of great differences in their vapor pressures(Table III), differences in the process variables originating from carbon number distribution of raw materials are relatively great in this process, especially in the oxidation step. A comparison is summarized in Table IV, which shows the disadvantage of a lower carbon number range to some extent.

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Table I Process Economics for C_{12-14} Secondary Alcohols and for Their 3-mole Ethoxylate

Raw Material and Utilities Consumption, (per ton of product)

	Alcohol	3-mole Ethoxylate
Normal Paraffins	1,240 kg	750 kg
Ethylene Oxide	----	420 kg
Other Chemicals	10,000 yen	8,000 yen
Steam	3.3 ton	3.0 ton
Fuel	----	----
Electric Power	500 kwh	400 kwh
Process Water	3.3 m^3	2.5 m^3
Cooling Water	600 m^3	500 m^3
Inert Gas	10 m^3	10 m^3

Commercial Installation

12,000 tons/yr of C_{12-14} Secondary Alcohols and 18,000 tons/yr of 3-mole Ethoxylate at Nippon Shokubai's Kawasaki Plant, Japan.

Table II Typical Example of Carbon Number Distribution of n-Paraffins Extracted from Kerosene

Carbon Number	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}
Distribution(%)	7	25	24	22	15	6	1

Table III Vapor Pressure and Boiling Point of n-Paraffins

Carbon Number	C_{11}	C_{13}	C_{15}
Vapor Pressure at 170°C(torr)	380	130	44
Boiling Point(°C)	196	235	271

Typical Physical and Surface Active Properties

To examine the physical and surface active properties of SAE, three secondary alcohol samples each having three successive carbon numbers, as mentioned earier, were prepared. For practical reasons, blends of alcohols are chosen instead of alcohols having individual carbon numbers. The alcohol samples were ethoxylated to various degrees of polymerization for testing. Two previous papers by other workers are recommended with reference to this subject. One by MacFarland(5) of Union Carbide Corp. deals with a blend of C_{11-15} secondary alcohols and the other by Matson(6) of Continental Oil Co. deals with individual carbon chain homologs.

Pour point, viscosity, cloud point, wetting power and foam properties, being important advantages of SAE, are presented here in comparison with other commercial products derived from primary alcohols (Ziegler and Oxo) or nonylphenol (branched chain).

Pour Point. Figure 3 shows pour points vs. Griffins' HLB value for various ethoxylated nonionics.

SAE, in general, have far lower pour points than those of primary alcohols(PA). Among three secondary alcohol series with different carbon number ranges, the lower the carbon number range, the lower the pour point, especially in the lower HLB or water-insoluble region.

Nonylphenol ethoxylates(NPE) have pour points similar to those of SAE in the higher HLB region but differ in the HLB region below 10.

Smith(7) and Fisher(8) recently published articles on the relationship of viscosity, pour point and alkyl chain length of primary alcohol ethoxylates(PAE) and SAE. The empirical equations proposed are in fairly good agreement with the authors' obser-

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Table IV Comparison of Process Variables with Different Carbon Number Ranges for the Production of Sec.-Alcohols

Factors	Carbon Number Range of n-Paraffins		
(Oxidation Step)	$C_{10} - C_{12}$	$C_{12} - C_{14}$	$C_{14} - C_{16}$
Reaction Temperature	Normal	Normal	Normal
Reaction Pressure	Higher	Normal	Lower
Conversion	Lower	Normal	Higher
Selectivity	Lower	Normal	Higher
Space Time Yield	Lower	Normal	Higher
(Separation and Purification Step)			
Distillation Temperature	Lower	Normal	Higher
Distillation Pressure	Lower	Normal	Higher
Manufacturing Cost	Higher	Normal	Lower

Table V Viscosity and Gel Range of Aqueous Surfactant Solutions

cP at 25°C

Surfactant		Surfactant Concentration (% by weight)									
		10	20	30	40	50	60	70	80	90	100
C_{10-12}SAE	(7EO)	2	7	28	75	98	94	84	77	65	50
"	(9EO)	2	5	18	68	151	142	112	97	81	64
"	(12EO)	2	6	28	118	221	221	171	134	114	94
C_{12-14}SAE	(7EO)	7	27	77	132	160	$3x10^3$	$1x10^4$	105	81	52
"	(9EO)	4	8	40	230	$1x10^3$	270	$7x10^3$	130	96	65
"	(12EO)	5	9	37	270	G E L		300	180	130	87
C_{14-16}SAE	(7EO)	3	23	74	135	162	$6x10^3$	$1x10^4$	100	77	52
"	(9EO)	2	6	35	218	$2x10^5$	258	$1x10^4$	123	93	61
"	(12EO)	2	6	30	229	G E L		227	176	126	87
C_{12+14}PAE	(7EO)	4	28	715	G E L			$5x10^4$	$1x10^5$	104	56
"	(9EO)	3	6	37	G E L			$2x10^3$	192	123	69
"	(12EO)	3	8	53	G E L				310	158	SOLID
N P E	(8EO)	167	292	421	597	$8x10^3$	$7x10^4$	$1x10^5$	$2x10^5$	274	232
"	(10EO)	4	32	320	G E L		$2x10^3$	$9x10^4$	404	290	257
"	(13EO)	2	6	40	G E L			882	408	306	279

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vations on SAE within the range of C_{10} to C_{16} and EO mole numbers of below 15. Their equations can be used to predict pour point or viscosity of SAE from their chemical structures.

Viscosity. Figure 4 shows plots of viscosity at 25°C vs. EO mole numbers for the three series of SAE. Here, the lower the carbon number range, the lower the viscosity.

PAE have much higher viscosities than SAE having the same carbon number range. Thus, the viscosity of C_{12+14} Ziegler PAE is about the same as that of C_{14-16} SAE except in the higher EO mole region, where PAE (12EO) is solid at this temperature. NPE have still higher viscosities than SAE.

As to the viscosity of aqueous solutions of nonionic surfactants, in general, gel formation tendency is very important. Table V and Figure 5 show differences in viscosity of aqueous solutions and gel ranges for various nonionics. Gel ranges of SAE are remarkably narrow compared with those of PAE and NPE(Table V).

Cloud Point. Figure 6 shows plots of cloud point against Griffins's HLB for various nonionics. As the cloud points of the three series of SAE are closely on a line within this HLB region, the cloud point of a SAE can be estimated from a curve made with other SAE having different alkyl carbon number ranges. PAE have higher cloud points than SAE at the same HLB. This might mean that secondary alkyls behave as stronger hydrophobes than do primary alkyls. NPE have different slopes of cloud point vs. HLB curves compared with alcohol ethoxylates.

Wetting Power. Figure 7 shows plots of wetting time against Griffin's HLB for various nonionics. Better wetting abilities of SAE compared with PAE are seen as in previous papers by MacFarland(5) and by Zika(9, 18).

Figure 8 shows temperature dependence of the wetting power of PAE, SAE and NPE each having about the same calculated HLB. It indicates a lower wetting power of PAE at lower temperatures and of NPE at higher temperatures compared with that of SAE.

Foam Properties. A previous paper(1) reported that SAE show better foam breakability than PAE or NPE. This tendency becomes clearer when SAE and PAE having lower carbon number ranges are compared. Figure 9 and Figure 10 show foam volume vs. concentration in an agitation test for C_{12-14} SAE (9EO), C_{10-12} SAE(9EO) anc C_{9+11} PAE(8EO) in the initial stage and after five minutes, respectively. Figure 11 shows the time required for 25% foam reduction vs. concentration of surfactant. In these figures, we can see that C_{10-12} SAE shows rapid foam reduction at lower or higher concentration. This should be a noteworthy phenomenon among various types of nonionic surfactants and can be applied in the formulation of easy rinsing detergents. A reason for such a maximum in the curves of foam volume vs. concentration has not yet been found.

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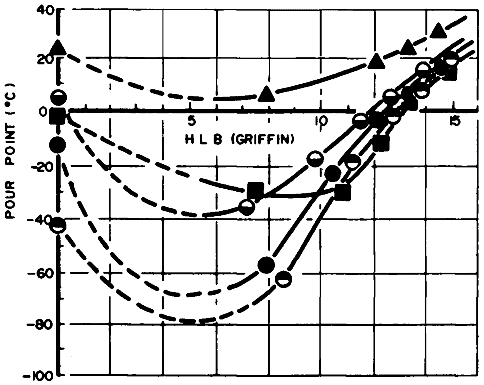

Figure 3. Pour point vs. HLB for various ethoxylated nonionics ((–◓–) C_{10-12} SAE; (–●–) C_{12-14} SAE; (–◒–) C_{14-16} SAE; (–▲–) C_{12+14} PAE (Ziegler); (–■–) NPE)

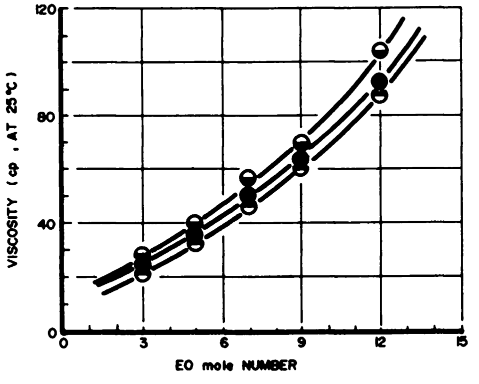

Figure 4. Viscosity vs. EO mole number for secondary alcohol ethoxylates ((–◓–) C_{10-12} SAE; (–●–) C_{12-14} SAE; (–◒–) C_{14-16} SAE)

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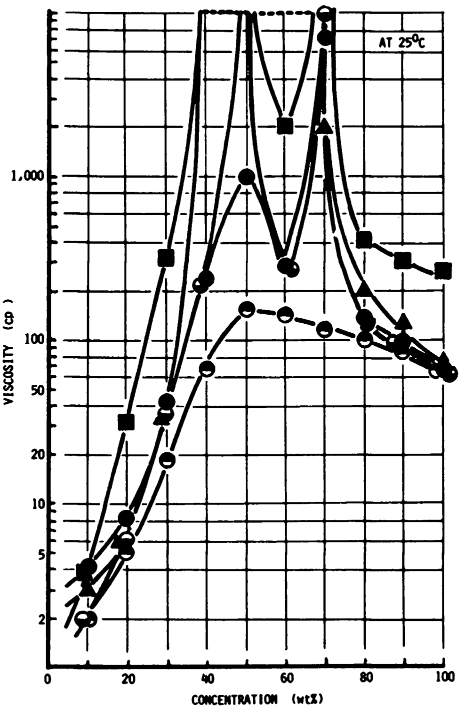

Figure 5. Viscosity vs. concentration for various ethoxylated nonionics ((–⊖–) C_{14-16} SAE (9EO); (–●–) C_{12-14} SAE (9EO); (–⊖–) C_{10-12} SAE (9EO); (–▲–) C_{12+14} PAE (9EO) (Ziegler); (–■–) NPE (10EO))

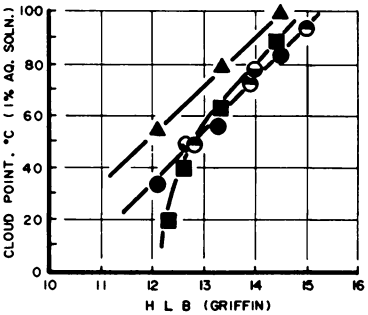

Figure 6. Cloud point vs. HLB for various nonionics ((–⊖–) C_{10-12} SAE; (–●–) C_{12-14} SAE; (–⊖–) C_{14-16} SAE; (–▲–) C_{12+14} PAE (Ziegler); (–■–) NPE)

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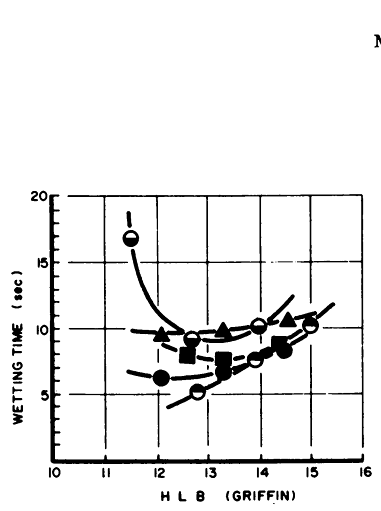

Figure 7. Wetting time vs. HLB for various ethoxylated nonionics. Test conditions: method—JIS-K-3362-1965; roller-cloth wool—10 × 90 mm; surfactant concentration—0.1 wt %; temperature—25°C. ((-◓-) $C_{10\text{-}12}$ SAE; (-●-) $C_{12\text{-}14}$ SAE; (-◒-) $C_{14\text{-}16}$ SAE; (-▲-) C_{12+14} PAE (Ziegler); (-■-) NPE)

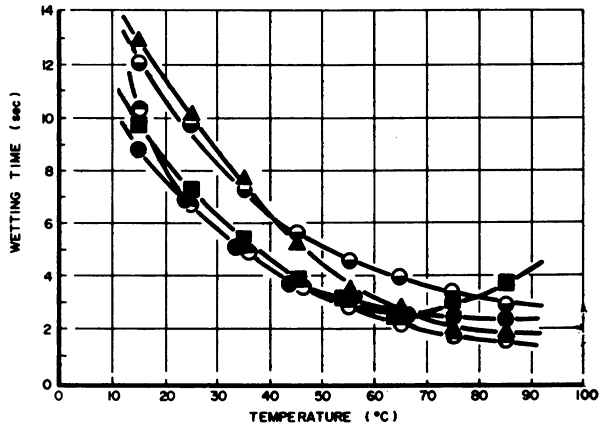

Figure 8. Wetting time vs. temperature for several nonionics. Test conditions: method—JIS-K-3362-1965; roller-cloth wool—10 × 90 mm; surfactant concentration—0.1 wt %. ((-◓-) $C_{10\text{-}12}$ SAE (8EO), HLB = 13.4, CP = 58°C; (-●-) $C_{12\text{-}14}$ SAE (9EO), HLB = 13.3, CP = 56°C; (-◒-) $C_{14\text{-}16}$ SAE (10EO), HLB = 13.2, CP = 54°C; (-▲-) C_{12+14} PAE (9EO), HLB = 13.3, CP = 79°C (Ziegler); (-■-) NPE (10EO), HLB = 13.3, CP = 63°C)

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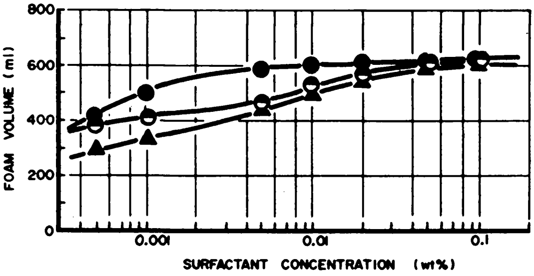

Figure 9. Effect of carbon number range on foam volume (initial stage) ((–◒–) C_{10-12} SAE (9EO); (–●–) C_{12-14} SAE (9EO); (–▲–) C_{9+11} PAE (8EO))

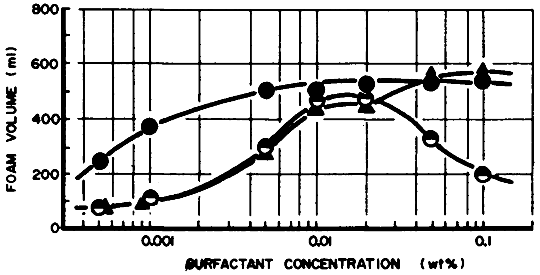

Figure 10. Effect of carbon number range on foam volume (after 5 min) ((–◒–) C_{10-12} SAE (9EO); (–●–) C_{12-14} SAE (9EO); (–▲–) C_{9+11} PAE (8EO))

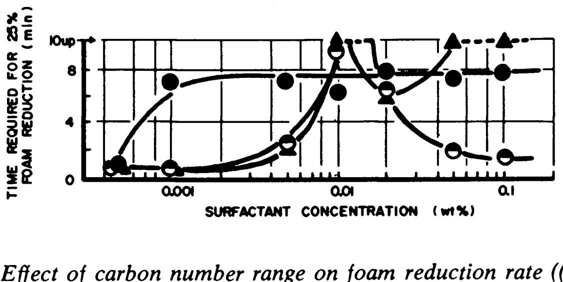

Figure 11. Effect of carbon number range on foam reduction rate ((–◒–) C_{10-12} SAE (9EO); (–●–) C_{12-14} SAE (9EO); (–▲–) C_{9+11} PAE (8EO))

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Good foam breakability of SAE having a lower carbon range may lead to excellent performance in detergent formulations which other surfactants have never shown.

Safety and Environmental Assessment

Biodegradability. The biodegradability of SAE has already been extensively examined by other workers using various test methods such as the standard BOD test, Shake-Culture test, Warburg test, River Die-away test, and Continuous Activated-Sludge test. All of these laboratory tests(10) showed rapid degradation of SAE. Several results obtained in the authors' laboratory have been reported, a summary of which follows.

a. River Die-away test(11). To examine biodegradation in natural rivers, water samples were taken from the upper, the middle and the lower regions of the Tama River, flowing along the border between two big cities, Tokyo and Kawasaki(Figure 12).

The biodegradabilities were followed by three analytical methods, i.e. (A) foam height method, (B) cobalt thiocyanate colorimetry (CTAS) and (C) COD (Cr) method.

Table VI shows the analytical data for the river water immediately after sampling. Although the sampling points were located within a distance of only about 30 km, the river water clearly showed different degrees of pollution. It seemed, therefore, very interesting to see how different bacterial populations and nutritive concentrations might affect the speed of biodegradation.

Three typical commercial samples tested are shown in Table VII. Figure 13, Figure 14 and Figure 15 show the test results obtained using the river water taken from Noborito, Fussa and Ohme, respectively.

Table VI River Water Used in the Test *(11)*

Sampling Point	Sampling Date	COD(Cr), ppm	CTAS, ppm	Foam, ppm
(1) Noborito	Apr. 21, '73	12	0	0
(2) Fussa	May 31, '73	4	0	0
(3) Ohme	Aug. 8, '73	0	0	0

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Table VII Nonionic Surfactant Samples Used in the River Die-away Test *(11)*

NPE(10EO)	Branched-chain nonylphenol 10 mole ethoxylate
PAE(9EO)	C_{12} - C_{15} Oxo alcohols (consisting of 60% straight- and 40% branched-chain) 9 mole ethoxylate
SAE(9EO)	C_{12} - C_{14} Secondary alcohol (consisting of all possible position isomers) 9 mole ethoxylate

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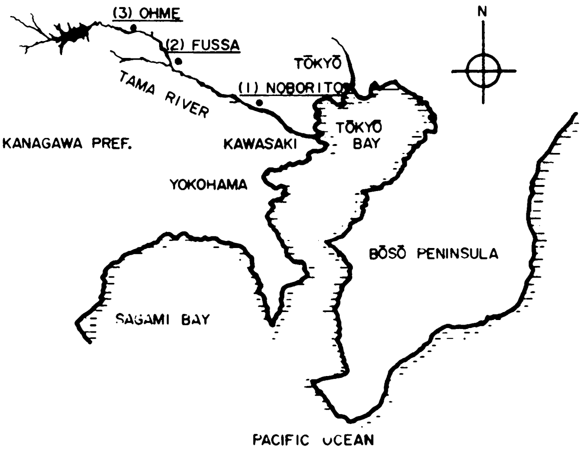

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*Figure 12. Map of the Tama River basin (*11*)*

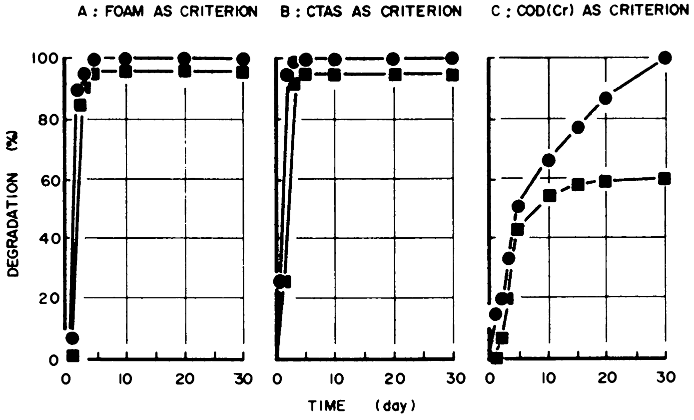

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Figure 13. Biodegradability of nonionic surfactants in river die-away test using the Tama River water, Noborito ((–●–) C_{12-14} SAE (9EO); (–■–) NPE (10EO)) *(*11*)*

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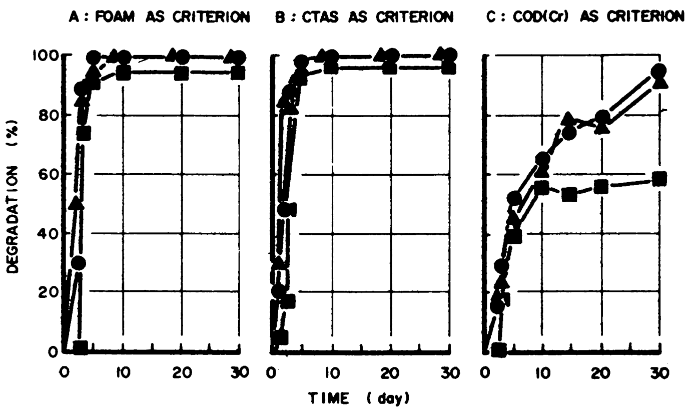

Figure 14. Biodegradability of nonionic surfactants in river die-away test using the Tama River water, Fussa ((–●–) C_{12-14} SAE (9EO); (–▲–) C_{12-15} PAE (9EO), (Oxo); (–■–) NPE (10EO)) (11)

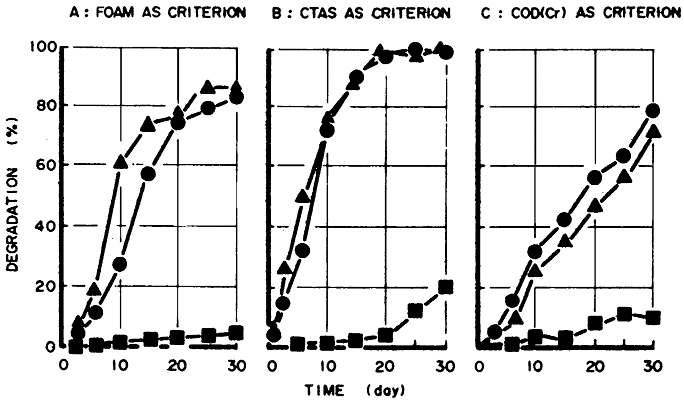

Figure 15. Biodegradability of nonionic surfactants in river die-away test using the Tama River water, Ohme ((–●–) C_{12-14} SAE (9EO); (–▲–) C_{12-15} PAE (9EO), (Oxo); (–■–) NPE (10EO)) (11)

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As seen in Figure 13, in river water from the lower regions, both SAE(9EO) and NPE(10EO) seemed to be degraded in a relatively short period, with no difference in foam height and with little difference by CTAS. However COD(Cr) measurements showed that about 40% of the NPE(10EO) remained undegraded after 10 days, and even over a prolonged period.

As seen in Figure 14, which shows data taken using river water from the middle regions, the rate of degradation was a little slower than in the lower regions in all three analytical measurements, with a tendency about the same as in the case of the lower regions. With regard to foam height and CTAS, PAE(9EO) and SAE(9EO) showed almost the same behavior. In the case of COD (Cr) measurements, the alcohol-based surfactants showed the same degradation rate while decomposition of NPE(10EO) did not exceed about 60%, as in the lower regions.

In Figure 15, which shows data from the upper regions, the Ohme, it is seen that, even in the case of foam height and CTAS, NPE(10EO) was resistant to decomposition. Thus, it was found that the NPE was extremely slow to be decomposed compared with alcohol-based nonionics, in the clean water of the upper regions. Moreover, even in the highly polluted water of the lower regions, it seemed to be decomposed only with regard to surface activity but never reached ultimate decomposition. On the contrary, alcohol-based nonionics, derived from both primary and secondary alcohols, seemed to be completely degraded in all cases..

The foregoing is in line with earlier work which showed that acclimated river water degraded an alkyl phenol ethoxylate when measured by foam volume reduction(11a).

b. Continuous-flow activated sludge test(12). This test was carried out to show that SAE is by far more easily degradable than NPE in a continuous-flow activated sludge system.

The apparatus used is the same as that adopted by Conway et al(13). The test was conducted over long periods at higher concentration of surfactants than in any previous studies. In the test, biodegradation was followed by measuring COD(Cr), COD(Mn), cobalt thiocyanate active substances (CTAS) and TOC(Figure 16). It was found that SAE(9EO), contrary to NPE(10EO), was adequately biodegraded by any measurements used, in spite of the high concentration of surfactant (200mg/l).

Toxicity to Fish(14). As to the relationship between surface activity and fish toxicity of surfactants, it is said that at a surface tension of water below 48 dynes/cm fish cannot breathe through their gills, resulting in fatal toxicity due to the changes in physical properties.

We examined the relationship between changes in surface tension and changes in toxicity and studied the toxicity of biodegradation intermediates of surfactants.

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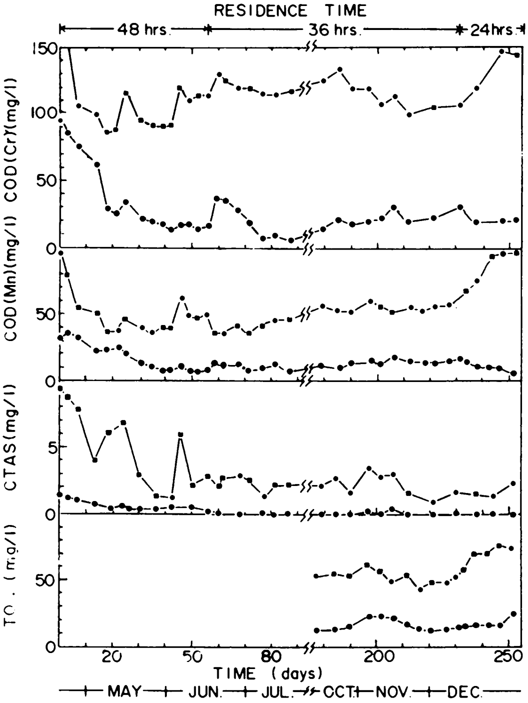

Test Conditions

Sample		NPE(10EO)	SAE(9EO)
Influent Composition			
Surfactant	(mg/l)	200	200
Urea	(mg/l)	25	25
Phosphoric Acid	(mg/l)	10	10
Ave. Anal. Value in Influent			
COD(Cr)	(mg/l)	339	406
COD(Mn)	(mg/l)	210	156
CTAS	(mg/l)	200	200
TOC	(mg/l)	120	123
Residence Time	(hrs)	48-24	48-24
MLSS	(mg/l)	2000±500	2000±500

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Figure 16. COD(Cr), COD(Mn), CTAS, and TOC remaining in continuous-flow activated sludge effluents fed 200 mg/L of NPE(10EO) or SAE(9EO) ((–●–) C_{12-14} SAE (9EO); (–■–) NPE (10EO)) (12)

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a. Acute toxicity (TLm48). Table VIII shows the test results for acute toxicity of various surfactants on gold fish.

The results show the same tendency as previously in that the stronger the surface activity, the stronger the toxicity, and the higher the ethylene oxide mole ratio, the lower the toxicity. TLm values obtained for secondary alcohol-based surfactants are also found to obey the known general rules. Macek and Krzeminski(14a) also reported a similar conclusion on acute effects of APE, PAE and SAE to bluegill sunfish by their static bioassays.

It is apparent that the toxicity of LAS is much stronger than that of ethoxysulfates derived both from primary and secondary alcohols.

Table VIII Acute Toxicity to Fish (14)

Surfactant	TLm(48hr), mg/l*
Nonioncs	
NPE(10EO)	5.4
C_{12-14} SAE(7EO)	3.3
C_{12-14} SAE(9EO)	5.1
C_{12-14} SAE(12EO)	12.0
C_{12} PAE(9EO)	1.9
C_{12-15} PAE(9EO)(60% straight/40% branched chain)	1.4
Anionics	
LAS	4.7
sec.-AES(Sulfate of C_{12-14} SAE(3EO))	43.0
prim.-AES(Sulfate of Lauryl Alc.-(2EO))	36.0

*Surfactant concn. to kill 50% of fish within 48 hr.
Method : Based on JIS-K-0102 Fish : 5 cm Goldfish

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b. Toxicity after biodegradation. Table IX and Table X are the results of preliminary tests of aquatic toxicity of various surfactants during their biodegradation in river water. Very high initial concentrations of surfactants were adopted here in order to clarify the differences in degree of toxicity reduction.

Table IX shows that 5 days aging of river water containing C_{12-14} SAE(9EO) or C_{12} PAE(9EO) can remarkably reduce their toxicity to fish even at the initial concentration of 20 mg/l, which corresponds to several times their TLm, and thus indicates that their toxicity tends to be reduced with their biodegradation

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Table IX Toxicity to Fish after 5d Biodegradation for Nonionic Surfactant (14)

Surfactant	Initial Concentration mg/l	% Fish Alive After 2h	After 24h	After 48h
SAE(9EO), C_{12-14}	20	100	90	70
PAE(9EO), C_{12}	20	100	100	60
NPE(10EO)	20	0	0	0
Control	0	100	100	90
NPE(10EO)	5	40	20	0

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Table X Toxicity to Fish After 5 and 10d Biodegradation for Anionic Surfactants (14)

Surfactant	Initial Concentration mg/l	% Fish Alive: 5d Biodegradation after 2h	after 24h	after 48h	10d Biodegradation after 2h	after 24h	after 48h
SAE(3EO)S[a]	100	100	90	90	100	100	100
	200	40	0	0	100	100	100
LAE(2EO)S	100	100	70	40	100	80	80
	200	0	0	0	0	0	0
LAS	100	0	0	0	0	0	0
	200	0	0	0	0	0	0
Control	0	100	100	90	100	100	100

a Sulfate of C_{12-14} Secondary Alcohol 3EO
b Sulfate of Lauryl Alcohol 2EO

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processes. On the contrary, NPE(10EO) shows no reduction in toxicity even at the initial concentration of 5 mg/l, suggesting that the toxicity of its biodegradation intermediates should be marked.

Table X shows similar results for anionic surfactants, in which no reduction in toxicity of LAS was observed but some reduction was found in the case of C_{12-14} SAE(3EO) sulfate and C_{12} PAE(2EO) sulfate especially at their initial concentration of 100 mg/l.

c. Surface tension and toxicity of biodegradation intermediates. Table XI shows the relationship between the ratio of live fish, surface tension and CTAS remaining after biodegradation. It indicates that both SAE(9EO) and PAE(9EO) have no toxicity at 3 - 4 mg/l CTAS remaining but NPE(10EO) still has strong toxicity at 2.8 mg/l CTAS remaining. Thus, it was found that the TLm_{48} values of both PAE and SAE after 4 days biodegradation in river water were 91 mg/l based on the initial concentration, and that of NPE was 3.7 mg/l (Table XII). In the case of NPE, the observed value, 3.7 mg/l, was lower than its original TLm_{48}. This means that the toxicity of its biodegradation intermediates should be higher than that of the original surfactant.

Figure 17 shows the surface tension after 4 days biodegradation vs. % live fish after 48 hrs. In the case of PAE and SAE, a surface tension of 48 dynes/cm after 4 days biodegradation was found high enough for fish to live, while in the case of NPE, 51 dynes/cm was found too low for fish to live. The results on NPE here are somewhat different from those of Macek and Krzeminski(14a), who reported that bluegill sunfish are probably less susceptible to the acute effects of APE than of AE in their dynamic bioassay conditions. They also reported in determining toxicity of the biodegradation products of four surfactants, including NPE(9EO), no mortality was observed even at an initial surfactant concentration ranging from 32 to 40 ppm. These differences might be explained by differences in biodegradation routes under different conditions and test procedures, or from differences in the alkyl structure of the NPE used.

Performance in Household Detergents

SAE now have a variety of applications in both household and industrial fields, some typical examples of which follow. Before going into details, some advantageous characteristics of SAE, which should be taken into account by users, are summarized in Table XIII.

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Table XI Toxicity of Biodegradation Intermediates of Nonionic Surfactants to Fish (14)

Nonionic Surfactant	Intial Concentration mg/l	Intial Surface Tension (dyne/cm)	CTAS After 4d Biodegradation (mg/l)	Surface Tension After 4d Biodegradation (dyne/cm)	% Fish Alive		
					After 24hr	After 48hr	After 72hr
C_{12-14} SAE(9EO)	35	33.9	0.4	58	100	100	100
	50	32.5	1.2	52	100	100	100
	75	31.5	3.7	48	100	100	100
	110	30.9	9.3	41	0	0	0
	160	30.9	18.2	38	0	0	0
C_{12-15} PAE(9EO) Oxo	35	34.2	0.3	60	100	100	100
	50	33.5	1.0	55	100	100	100
	75	33.0	2.9	48	100	100	90
	110	32.8	6.5	42	10	0	0
	160	32.7	15.0	38	0	0	0
NPE(10EO)	2	53.2	1.0	63	100	100	100
	3	51.1	1.8	57	100	100	80
	4.5	49.0	2.8	51	20	0	0
	6.5	47.0	3.9	47	0	0	0
	9.5	45.1	6.0	40	0	0	0

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Table XII TLm (48hr) of Biodegradation Intermediates Calculated from Initial Surfactant Concentration (14)

Surfactant	Original TLm(48hr) (mg/l)	TLm (48hr) After 4 Day Biodegradation* (mg/l)
SAE(9EO)***	5.1	91
PAE(9EO)**	1.4	91
NPE(10EO)	5.4	3.7

* Initial surfactant concentration to kill 50% of the fish within 48 hr.

** C_{12-15} Oxo-alcohol 9 mole ethoxylate, consisting of 60% straight - and 40% branched - chain

*** C_{12-14} Secondary alcohol 9 mole ethoxylate, consisting of all possible position isomers

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Table XIII Characteristics of Secondary Alcohol Ethoxylates

Properties	Advantageous Effects
Low Pour Point Low Viscosity	→ Easy Handling
	↕
High Solubility Narrow Gel Range	→ Easy Liquid Formulation
Good Wetting Power Good Foam Breakability	→ High Performance
Good Biodegradability	→ Easy Waste Treatment
Containing no Free Alcohol	→ Odorless

Detergency - HD Laundry Application. To evaluate the detergency of three series of SAE, each having a different carbon no. range, typical Terg-O-Tometer tests were run on artificially soiled cotton and polyester/cotton. Test conditions and soil type are summarized in Table XIV. The results are shown in Figure 18 and Figure 19. As seen in these figures, the higher the carbon number range of SAE, the higher the detergency. This tendency is interesting if applied to low or no phosphate detergents. But it should be noted that the detergency obtained here represents removal of clay-based soil. In removal of more oily soil, the tendency may be somewhat different.

Figure 20 shows detergency vs. EO mole unit for C_{12-14} SAE with or without builder. It is seen that the builder has considerable efficiency in removal of clay-based soil.

Figure 21 shows a comparison of detergency of SAE(9EO) and LAS at different STPP concentrations. This result is also interesting in the formulation of non-built liquid detergents.

More detailed studies on detergency of SAE of single carbon no. chain ranging from C_{10} to C_{16} were made by Matson(6). From his studies, it can be said that an optimum choice of SAE in non-built HDL should be in the range C_{12-14} with 60 - 64% EO (7 - 9EO).

An interesting test result on the removal of mineral oil from a polyester substrate was reported by Dillan et al (15). This suggests that SAE has much higher detergency for polyester fabric than PAE at lower temperatures.

Detergency in Dish Washing. Detergency tests for dish washing were conducted by the Modified Leenerts test prodecure. The test conditions and apparatus are shown in Table XV.

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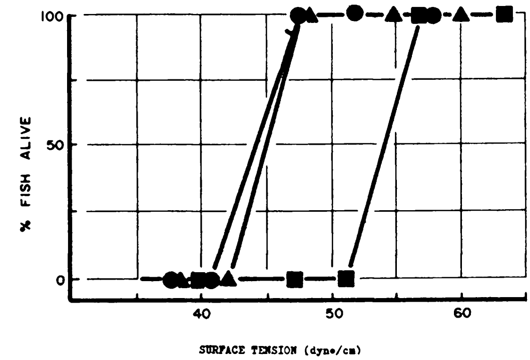

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Figure 17. The % fish alive (48) vs. surface tension after 4 day biodegradation ((-●-) C_{12-14} SAE (9EO); (-▲-) C_{12-15} PAE (9EO), (Oxo); (-■-) NPE (10EO)) (14)

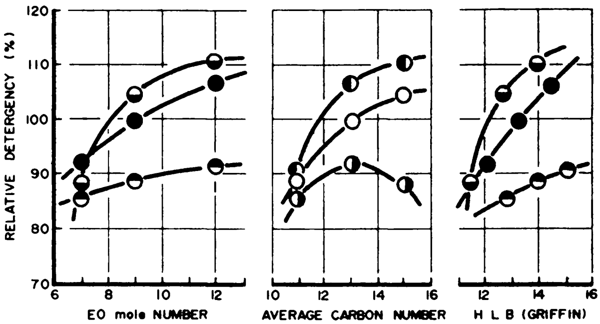

Figure 18. Relationship between carbon number range and detergency for cotton broadcloth. Test condition: surfactant concentration—0.03 wt %. ((-◓-) C_{10-12} SAE; (-●-) C_{12-14} SAE; (-◒-) C_{14-16} SAE; (-◑-) SAE (7EO); (-○-) SAE (9EO); (-◐-) SAE (12EO))

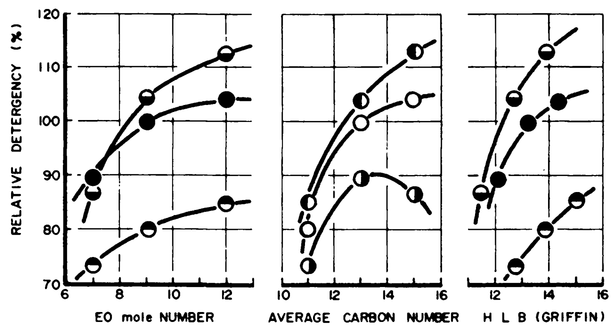

Figure 19. Relationship between carbon number range and detergency for polyester/cotton broadcloth. Test condition: surfactant concentration—0.03 wt %. ((-◓-) C_{10-12} SAE; (-●-) C_{12-14} SAE; (-◒-) C_{14-16} SAE; (-◑-) SAE (7EO); (-○-) SAE (9EO); (-◐-) SAE (12EO))

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Table XIV Terg-O-Tometer Test Conditions

Temperature	25 ± 2°C
Agitation Speed	100 rpm
Washing Time	5 min.
Rinsing Time	5 min.
Water Hardness	50 ppm
Liquid Volume/Pot	1 Liter
Size of Cloth Swatch	10 X 10 cm
Fabric Load/Pot	3 Swatches
Reflectance of Soiled Swatch	Rs = ca. 50%
Points of Rs Detection	3

Soil Composition ; (A) : (B) : (C) = 0.5 : 49.75 : 49.75

(A) Carbon : Standard of the Japan Oil Chemists' Society

(B) Inorganic Component : The Kanto District Loam, 250 Mesh Passed

(C) Organic Component :

Organic Soil Components,	wt%
Myristic Acid	16.7
Oleic Aicd	16.7
Tristearin	16.7
Triolein	16.7
Cholesterol	8.8
Cholesteryl Stearate	2.2
Paraffin Wax(mp:50-52°C)	11.1
Squalene	11.1

Soil Penetration ; Modified Supersonic Wave Method Using CCl_4 as Solvent

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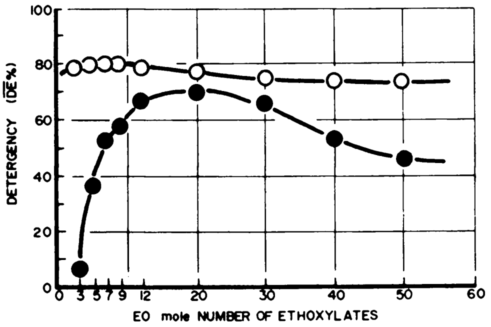

Figure 20. Detergency of C_{12-14} secondary alcohol ethoxylates with or without builders. Test conditions: surfactant concentration—0.03 wt %; builder concentration—0.12 wt %; builder composition: STPP—20 wt part; Na_2CO_3—5 wt part; sodium metasilicate—10 wt part; Na_2SO_4—20 wt part; CMC—1 wt part. ((–●–) C_{12-14} SAE alone; (–○–) C_{12-14} SAE and builder)

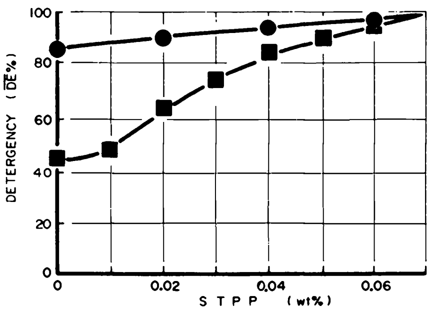

Figure 21. Effect of STPP on detergency. Test condition: surfactant concentration—0.03 wt %. ((–●–) C_{12-14} SAE (9EO); (–■–) LAS)

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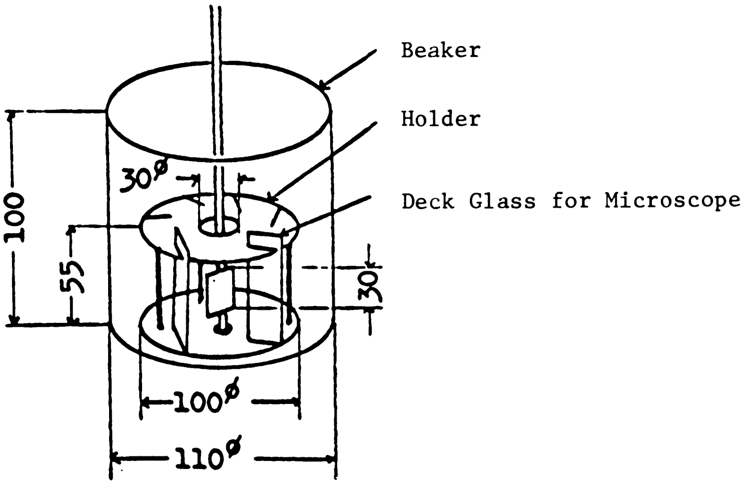
Table XV Modified "Leenerts" Test Conditions

Water Temperature		25°C
Agitation Speed		600 rpm
Wash Time		3 min.
Rinse Time		1 min.
Water Hardness		40 ppm
Detergent Solution/Beaker		700 ml
Detergent Concentration		0.04 %
Weighing		After 1.5 hr. Exposure to Air
Soil Volume/Deck Glass		23 - 27 mg
Composition of Soil Solution;		
	Soybean Oil	15 parts
	Tallow	15
	Chloroform	100
	Oil Red	0.1
Soiled Deck Glass Preparation		Deck Glasses were Immersed in Soil Solution Kept at 10±0.5°C and Dried for 12 hr.



Contrary to the case of heavy-duty detergency, the results show comparable detergencies of C_{10-12} and C_{12-14} SAE at an optimum EO mole number of about 7(Figure 22). Figure 23 shows the detergency of SAE and LAS at relatively high concentration levels. SAE(7EO), in contrast to LAS, shows detergency increasing in proportion to increased concentration. This would be of interest if applied to cleaners for heavily soiled surfaces such as kitchen ventilators. Reverse effects observed in the case of SAE(3EO) should be due to adsorption of surfactant on the soil. This means that SAE(3EO) can affect the swelling of hard oil.

Some synergistic effects were observed in binary systems consisting of LAS and SAE or SAE sulfate. Figure 24 gives the results of this study. Optimums lie between 50 and 75% of LAS in all three cases.

Viscosity and Clear Point Behavior in Liquid Formulation. SAE, as mentioned earlier, generally have the following advantageous characteristics, i.e. low viscosity, low pour point and high solubility. These properties lead to easy liquid formulation even at very high concentration. Flammer(16) pointed out this advantage in connection with the required amount of hydrotropes and concluded that SAE is far more economical a raw material for HDL than PAE.

Here, as an example, viscosity and clear point behavior of a ternary system containing LAS, C_{12-14} SAE(12EO) and water are shown in Figure 25 and Figure 26. It can easily be seen how a liquid detergent of very high concentration can be obtained.

Calcium Ion Sequestering Ability. To prevent eutrophication of surface water, it might be better to lower the phosphate content in detergents. On the other hand, due to the structure of washing machines and washing habits in Japan, high foam detergents are preferred from the commercial view point. In order to keep detergents high foaming, anionics are necessary. Another important point to be tested, beside foaming, is calcium ion sequestering ability. This ability was measured by the modified Murata and Arai's procedure(17) for C_{12-14} SAE in combination with various anionics.

The results are shown in Figure 27. It can be seen the all the anionics tested show significant effects of the combination with SAE on their sequestering ability. For this effect, the optimum EO mole number for each anionic is different. Since the combination of LAS with STPP gives a calcium ion sequestering ability of only 165 mg/g-detergents by this procedure, the combination of SAE with LAS(Linear Alkyl-benzene Sulfonate), AOS (α-Olefin Sulfonate), SAS(Secondary Alkane Sulfonate) or SDS (Sodium Dodecyl Sulfate) would be recommended for use in heavy-duty detergents.

The relationship between calcium sequestering ability and detergency or redeposition of soil is now being investigated in the authors' laboratory.

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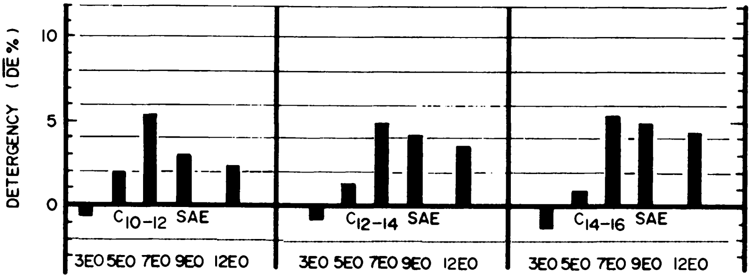

Figure 22. Dish washing detergency of SAE in modified "Leenerts" test

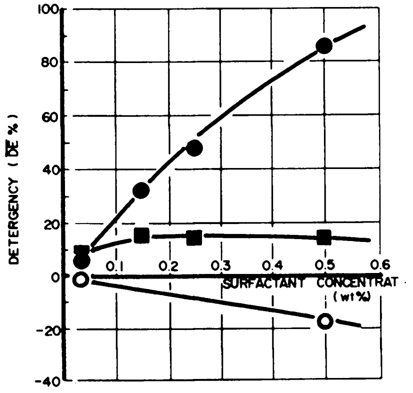

Figure 23. Concentration effect of surfactant in modified "Leenerts" test ((–●–) C_{12-14} SAE (7EO); (–O–) C_{12-14} SAE (3EO); (–■–) LAS)

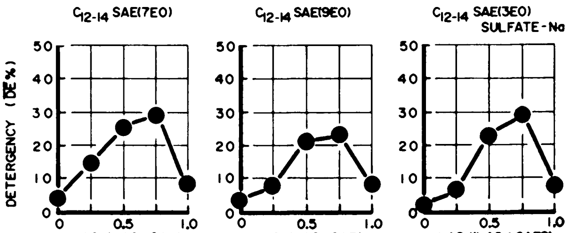

Figure 24. Synergistic effect on detergency in binary surfactant systems (test method: modified "Leenerts"; condition: total surfactant concentration—0.04 wt %)

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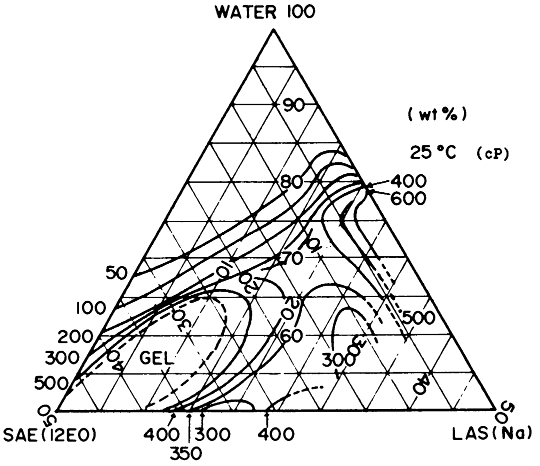

Figure 25. Viscosity of liquid detergent based on C_{12-14} SAE(12EO), LAS(Na), and H_2O

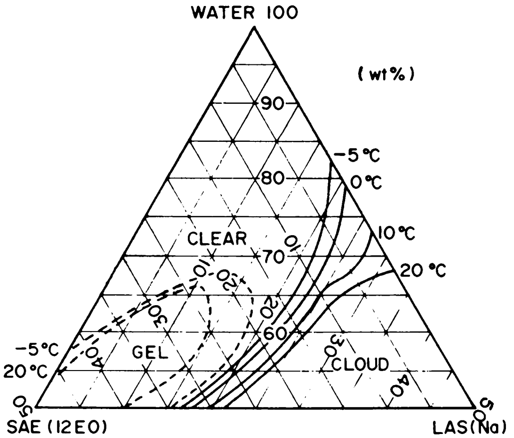

Figure 26. Clear point of liquid detergent based on C_{12-14} SAE(12EO), LAS(Na), and H_2O

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Industrial Applications

SAE can be generally utilized as biodegradable detergents or surfactants for many industries in which the conventional alkylphenol ethoxylates have been used.

Textile Industry. Several papers dealing with applications of SAE in textile processing were already published by Zika of Union Carbide Corp.(9, 18) and Rein of Continental Oil (19). Some additional performance data obtained in the authors' laboratory follow.

One example is the raw wool scouring process. The 7 mole ethoxylate of C_{12-14} secondary alcohol has excellent grease removal efficiency when used in raw wool scouring operations, as seen in Figure 28. Because of the unusually soft hand resulting, it is now used widely in Australia.

In cotton scouring, SAE also exhibits detergency comparable to that of the conventional nonylphenol ethoxylates as in Figure 29.

Not only in detergency but also in rewetting and in rinsability, SAE gives satisfactory performance. Figure 30 shows rewetting data demonstrating that SAE, over all the carbon number ranges tested, i.e. C_{10-12}, C_{12-14} and C_{14-16}, give better rewetting than nonylphenol ethoxylates.

Good rinsability of SAE has already been proven by Rein(19). SAE rinses from cotton, polyester/cotton and polyester/wool fabrics as easily as alkylphenol ethoxylate surfactants.

When choosing EO mole ratios of SAE for textile wet processing, one should consider the cloud point elevation at reduced surfactant concentration, which is seen in alcohol ethoxylates in general. For example, Figure 31 shows different clouding regions at different concentrations of SAE and nonylphenol ethoxylates having relatively low cloud points. The 7 mole ethoxylate of C_{12-14} secondary alcohol has its nominal cloud point at 34°C at 1% concentration. Thus, SAE(7EO) can be used at a temperature far above its nominal cloud point, giving better performance. This kind of effect is larger in SAE than in NPE.

In order to be used as an additive in various types of textile lubricants, surfactants should have high miscibility with base oils as well as the other fundamental surfactant characteristics such as lubricity improving ability and antistatic properties. Table XVI shows the miscibility of C_{12-14} SAE in various lubricant base oils in comparison with that of NPE(10EO). Good miscibility of SAE can be seen in the Table. Further information, including practical examples, is contained in Union Carbide Corp.'s booklet on Tergitol 15-S nonionics(20).

Some patent literature (21, 22, 23) disclose that secondary alcohol esters, with or without ethylene oxide chains on the

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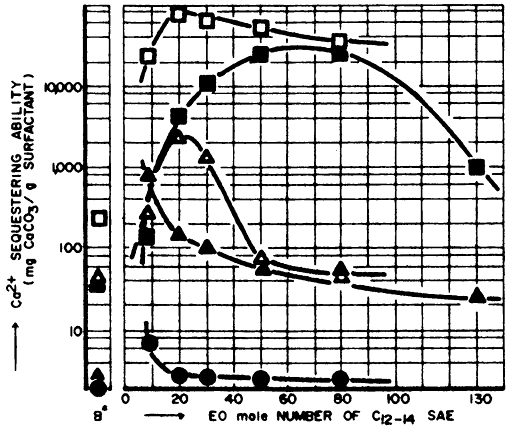
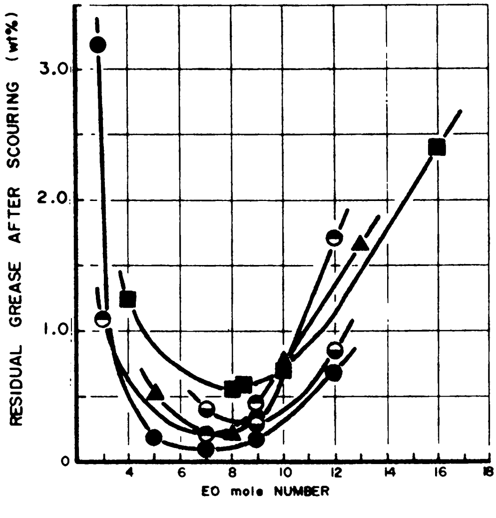


Figure 27. Calcium ion sequestering ability of $C_{12\text{-}14}$ secondary alcohol ethoxylates in combination with an anionic surfactant. Test conditions: surfactant concentration: nonionics—0.1 wt %; anionics—0.1 wt %; B = without nonionics (blank). ((–●–) with sodium laurate; (–▲–) with SDS; (–△–) with SAS; (–■–) with LAS;(–□–) with AOS)*



Test Conditions :

System : 4 - Bowl Scouring, with Alkaline Builder

Stage	1	2	3	4
Liquor Volume (l)	1	1	1	1
Na_2CO_3 Conc. (wt%)	0.2	0.1	0	0
Surfactant Conc. (wt%)	0.1	0.2	0.2	0

Water Temperature: 50 °C

Immersion Time: 2 min. in Each Bowl

Raw Wool: AGA-79, Australia (13.9 % Grease in Unscoured) 5 g x 5 skeins

Figure 28. Wool scouring efficiency of ethoxylates ((–◒–) $C_{10\text{-}12}$ SAE; (–●–) $C_{12\text{-}14}$ SAE; (–◓–) $C_{14\text{-}16}$ SAE; (–▲–) $C_{12\text{-}13}$ PAE (Oxo); (–■–) NPE)

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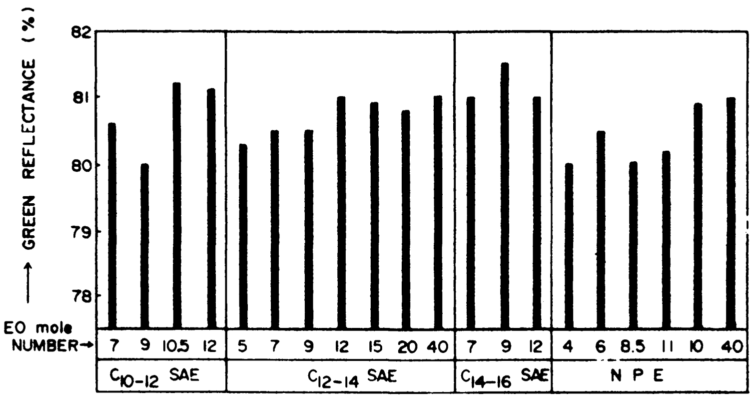

Figure 29. Cotton scouring efficiency of ethoxylates (test conditions: apparatus—Terg-O-Tometer; water temperature—80°C; agitation speed—95 rpm; scouring time—60 min; rinse time—30 min; surfactant concentration—0.2 wt %; NaOH concentration—4.0 wt %; liquor volume—1.0 L; reflectance before scouring—74.3%)

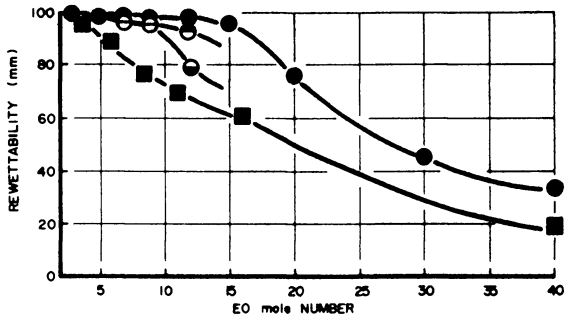

Figure 30. Rewetting data. Capillary rise method: U. Baumgarte: Melliand Textilberichte, 49, *1306 (1968). (mm): height of the elevation of test solution. ((–⊖–) C_{10-12} SAE; (–●–) C_{12-14} SAE; (–⊖–) C_{14-16} SAE; (–■–) NPE)*

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In Monohydric Alcohols; Wickson, E.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1981.

Publication Date: June 15, 1981 | doi: 10.1021/bk-1981-0159.ch009

Table XVI Miscibility of C_{12-14} Secondary Alcohol Ethoxylates in Various Lubricant Base Oils

	C_{12-14} Sec. Alcohol Ethoxylates					Nonylphenol
	3EO	5EO	7EO	9EO	12EO	10EO
(At 30°C)						
Water	C	B	A	A	A	A
Spindle Oil	A	A	A	A	C	C
Liquid Paraffin	A	B	C	C	C	C
Butyl Stearate	A	A	A	A	A	A
Methyl Oleate	A	A	A	A	A	A
Dioctyl Sebacate	A	A	A	A	A	A
Rapeseed Oil	A	A	A	A	B	C
(At 60°C)						
Coconut Oil	A	A	A	A	A	B
Tallow Oil	A	A	A	A	B	C
Triglyceryl Stearate	A	A	A	A	A	A

A = Miscible B = Dispersed or Emulsified C = Immiscible

Base Oil/Surfactant = 80/20

alcohol, are useful in fiber treating processes because of their low pour points, high smoke points, low volatilities at high temperature and low coefficients of fiber to metal friction. Typical examples are the stearate of C_{11-15} SAE(3EO) (21) and benzoate of C_{12-14} SAE(3EO) (22).

Pulp and Paper Industry. The pulp and paper industry is another area in which SAE can be widely utilized. In the deresination of pulp, C_{12-14} SAE are suitable biodegradable surfactants to replace alkylphenol ethoxylates.

Table XVII is an example of the test result showing comparable efficiency of SAE, PAE and alkylphenol ethoxylates in resin removal from sulfite pulp. A Japanese patent specification(24) by Lion Fats and Oils describes 10-16 mole ethoxylates of C_{8-15} secondary alcohols as extremely useful in deresination of pulp, especially in the manufacture of dissolved pulp for the rayon industry. According to the patent specification, C_{12} to C_{14} alkyls give the best results among 12 mole ethoxylates; ethoxylates of from 10 to 13 moles of EO can give the best results among other ethoxylates of C_{12-14} secondary alcohols, and the optimum amount of SAE(12EO) is in the range between 0.2 and 0.6% by weight based on pulp.

Another Japanese patent(25) to Lion Fats and Oils claims the use of SAE in combination with Pluronic® type nonionics in the deresination process.

EO/PO adducts of secondary alcohols are also attractive surfactants in this application field. SAE and also EO/PO adducts of secondary alcohols are efficiently used in paper machine felt washing. In this case, their low foaming properties give advantageous effects. They are also being used in combination with nonylphenol ethoxylates to reduce the load on biochemical treatment of waste effluents. A mixture consisting of 25% SAE(12EO) and 75% NPE(10EO) also gives synergistic effects in the deresination of pulp.

Miscellaneous. Nonionic surfactants, in general, have wide and highly fragmented application areas. Each type finds preference depending on the individual industry. SAE also have many miscellaneous applications in which their characteristics are advantageously utilized.

Several interesting recent patent literature references are illustrated as follows:

a. Emulsifiers for agricultural chemicals(26)
   Example : C_{12-14} SAE(8EO) for emulsifying machine oil
   Effects : 1. Good surface tension lowering
   2. High wetting power
   3. Stable emulsion

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b. Emulsifiers for emulsion polymerization of vinyl monomer (27)
Example : C_{12-18} SAE(50EO) for the emulsion polymerization of ethyl acrylate
Effects : Chemically and mechanically stable emulsified resin products

c. Spreaders for agricultural chemicals (28)
Example : C_{12-14} SAE(7EO) 20 parts by weight
Oleic acid(5EO) 10 "
Methanol 20 "
Water 50 "
Effects : 1. Low surface tension
2. High wettability
3. Sharp contact angle

d. Water soluble quenching agents for metal hardening (29)
Example : C_{12-14} SAE(15EO) 5 parts by weight
Water 95 "
Effects : 1. Efficient cooling ability
2. Small effect of concentration on cooling ability

SAE could be expected to be utilized in Enhanced Oil Recovery, because their low interfacial tension and low interfacial viscosity might be predicted. Finally, emulsion breakers for crude oil may be another interesting application of SAE.

Derivatives of Secondary Alcohol Ethoxylates

Propylene Oxide Adducts. SAE, in general, have better foam breakability among the nonionics, presumably due to the secondary alkyl structure and narrow distribution of EO chain lengths. Besides, modification of nonionics by the addition of propylene oxide (PO) to the terminal hydroxyl group generally reduces the foaming capacity(30). The addition of PO to SAE may, therefore, lead to nonionics with low and fast breakable foams.

The foam behavior of EO/PO adducts of secondary alcohols, primary alcohols and nonylphenols is shown in Figure 32. It can be seen that the best foam breakability is with SAE(7EO)(4.5PO), among the three.

PO adducts of SAE having various degrees of polymerization of EO and PO have been widely used in both household and industrial application areas where low and fast breaking foam is required. Textile scouring, machine felt washing in the paper industry, industrial hard surface cleaning, and machine dish washing (both in washing and in rinsing) are the main application areas so far.

Furthermore, as the combination of SAE with PO adduct of SAE gives a very low viscosity index, it can be effectively used where

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Table XVII Deresination of Pulp Using Nonionic Surfactant

Test Condition : Pulp = LDSP, After Mild Alkaline Extraction, Water=64%, Resin=0.86%*, Pulp Concentration=10%, Alkali Concentration=2%, Temp.=100°C, Time=90min.

Surfactant	Surfactant Concentration* (%)	Resin Content After Treatment* (%)	Resin Removal** (%)
-	-	0.441	48.7
C_{12-14}SAE(9EO)	0.1	0.427	50.4
	0.2	0.378	56.0
	0.3	0.316	63.3
C_{12-14}SAE(12EO)	0.1	0.413	52.0
	0.2	0.335	61.0
	0.3	0.256	70.2
C_{12-15}PAE(9EO) (Oxo Alcohol)	0.1	0.434	49.5
	0.3	0.323	62.4
Nonylphenol(10EO)	0.1	0.405	52.9
	0.2	0.326	62.1
	0.3	0.236	72.6
Octylphenol(10EO)	0.3	0.298	65.3

* Based on Dry Pulp

** 100 X (0.86 - % Resin After Treatment) / 0.86

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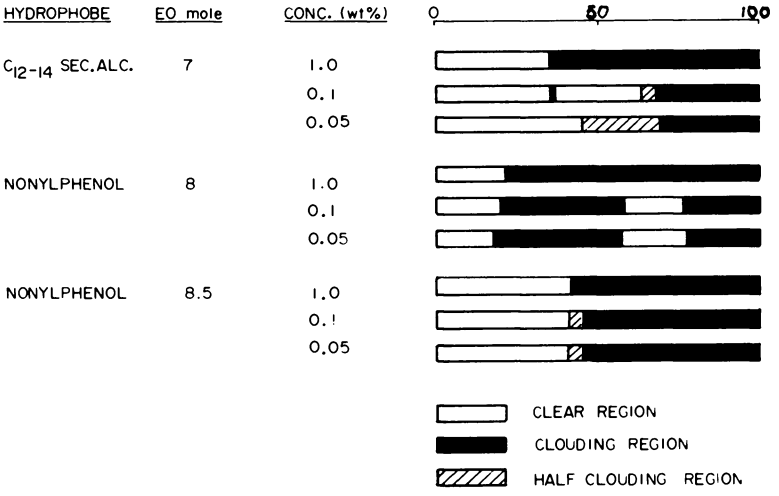

Figure 31. Cloud point of ethoxylates at reduced concentrations

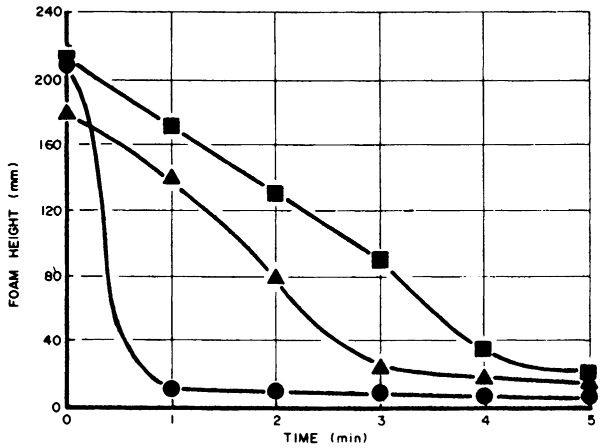

Figure 32. Foam properties of propylene oxide adduct of secondary alcohol ethoxylate compared with those of others. Test conditions: method—Ross-Miles (JIS-K-3362); surfactant concentration—1.0 wt %; water temperature—25°C. ((-●-) C_{12-14} SAE (7EO) + (4.5PO); (-▲-) C_{12+14} PAE (7EO) + (4.5PO); (-■-) NPE (8EO) + (4.5PO))

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automatic flow or volumetric control is necessary. The applicable fields will surely be widened.

Ethoxysulfates. It is said that there are some difficulties in producing ethoxysulfates from SAE by conventional sulfation techniques using sulfur trioxide or chlorosulfonic acid, mainly due to the low yield and unpleasant odor of the product (31). Detergent formulators, therefore, have hesitated to use this material.

Nippon Shokubai's modified ammonium sulfamate method, however, can improve the product quality and the reaction yield. A yield of above 99% can be obtained and the resulting product is almost odorless with excellent stability. Skin irritation is much less compared with the product made by chlorosulfonic acid because of the low level of impurities found owing to the mild reactant. See (Table XVIII).

The application possibilities have thus been widened.

Table XVIII Skin Irritation Levels of SAE-sulfates Made by Different Sulfonating Agents*

Sample	Sulfonating Agent	Conc. (%)	pH	Skin Irritation: Draize's Score: Erythema & Eschar	Edema	Net Rating**
SAE sulfate(Na)	HSO_3Cl	20	7.2	2 - 8	0 - 3	C
SAE-sulfate(NH_4)	NH_2SO_3H	20	5.8	0	0 - 6	B
SAE-sulfate(Na)	"	20	6.8	0	0 - 5	B

* These data were provided by Y. Yanagimoto (The Life Science Laboratory)

** A = None, B = Mild, C = Moderate, D = Severe. See Table XX.

Sulfosuccinate Half Esters. To meet the demand for surfactants having low toxicity, especially low skin irritation, Nippon Shokubai commercialized a series of sulfosuccinate half esters of SAE, SOFTANOL-MES series, by it's own technology(32, 33, 34).

Figure 33 shows the synthetic route. The intermediate, sodium maleate half ester, is relatively easily hydrolyzed in water, while the end product, disodium sulfosuccinate half ester, is not appreciably hydrolyzed in water in either acidic or neutral condition (Figure 34).

The surface tension lowering effects of this type of anionic are relatively weak, and their CMC values are a little higher than those of ordinary anionics (Table XIX). Their foaming ability is much higher than the original SAE (Figure 35), while their wetting power is lower than LAS (Figure 36). Their calcium sequestering

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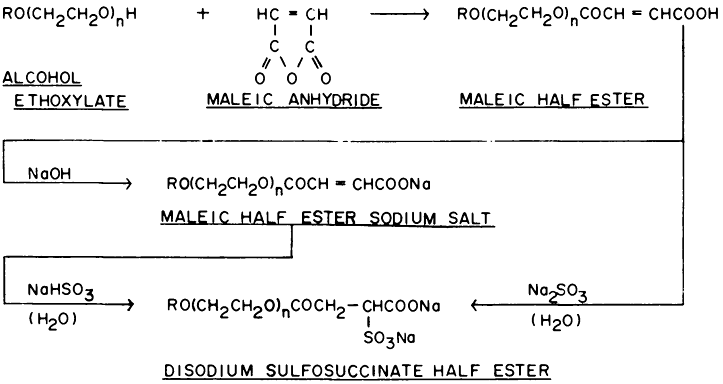

Figure 33. Synthetic route to disodium sulfosuccinate half ester

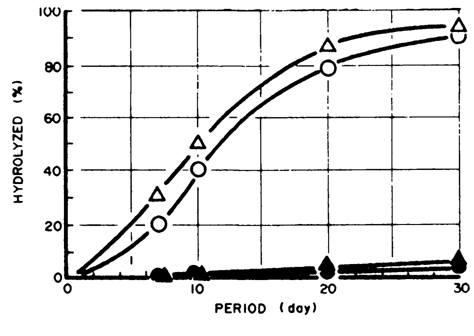

Figure 34. Hydrolysis rate of sodium maleate half ester and disodium sulfosuccinate half ester of SAE. Test conditions: surfactant concentration—5 % aq. soln.; temperature—40°C; initial pH—7.0. ((–○–) sodium maleate half ester of C_{12-14} SAE (3EO); (–△–) sodium maleate half ester of lauryl alcohol 3EO; (–●–) disodium sulfosuccinate half ester of C_{12-14} SAE (3EO); (–▲–) disodium sulfosuccinate half ester of lauryl alcohol 3EO)

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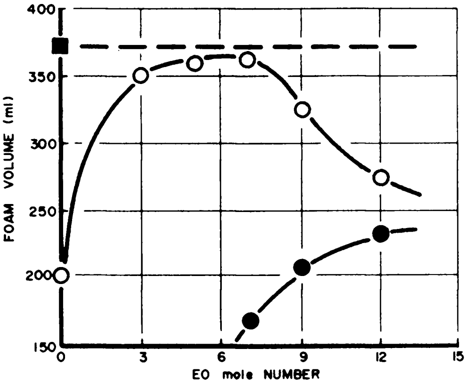

Figure 35. Initial foam volume of disodium sulfosuccinate half ester of C_{12-14} secondary alcohol ethoxylates. Test method: agitation method: surfactant concentration—0.1 %; surfactant solution—100 mL; water temperature—25°C; agitation speed—3500 rpm; agitation time—2 min. ((–○–) disodium sulfosuccinate half ester of C_{12-14} SAE series (SFT-MES-series); (–●–) C_{12-14} SAE; (–■–) LAS)

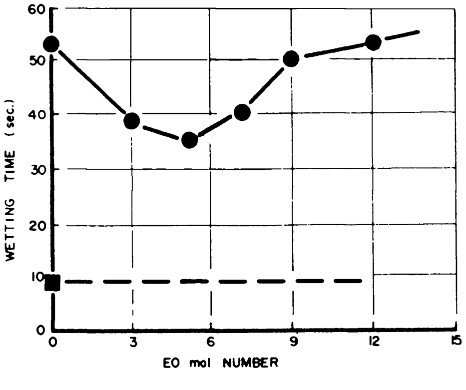

Figure 36. Wetting power of disodium sulfosuccinate half ester of C_{12-14} secondary alcohol ethoxylates (SFT-MES-series). Test conditions: surfactant concentration—0.1 wt %; cloth—wool. ((–●–) SFT-MES-series; (–■–) LAS)

ability increases with increasing EO mole number, approaching to about the same level as the original SAE (Figure 37). This ability of LAS, SDS, sodium laurate and other anionics is significantly increased when combined with a sulfosuccinate of SAE(Figure 38). For this effect, the optimum EO mole number for each anionic is different.

In spite of their relatively high surface tension and poor wetting power, detergency tests show their better performance than LAS in non-built and comparable performance to LAS in built systems (Figure 39).

The toxicological data for the sulfosuccinate esters are summarized in Table XX. Products of this type in general show low toxicity and low irritation. Eye irritation decreases with increasing EO mole number, approaching the non-irritating level. Further, both skin and eye irritation of AES (Sulfate of C_{12} PAE) can be significantly weakened when mixed with the sulfosuccinate (Table XX). This effect may suggest their applicabilities in personal care products such as hair or body shampoo, baby soap and medical soap.

Aquatic toxicity is also reduced when a SAE is converted to its sulfosuccinate. Fish toxicity, TLm_{48}, of C_{12-14} SAE(7EO) changes from 8 to 118 ppm with conversion into its sulfosuccinate.

In addition to their low toxicity and irritation, sulfosuccinates of SAE may be recognized as anionic surfactants having nonionic properties and performance. Their wide application, therefore, should be considered.

Postscript

Nowadays, it is believed worldwide that n-paraffins, which are extracted from kerosene, will be more advantageous raw material than ethylene from naphtha cracking in view of both resource saving and process economics.

A problem to be solved for surfactant range alcohols based on n-paraffins is how to utilize all n-paraffins in crude oil, which have wide carbon number ranges, by finding effective applications of the products therefrom.

As to the industrial surfactants, the shortage of sperm alcohol, due to the restrictions on whale fishing, has increased the demand for longer carbon chain alcohols.

In household detergents, owing to the controls and restrictions on phosphate builders, a growing demand for lime dispersing and high detergency surfactants will necessitate increased production of alcohol ethoxylates having relatively high carbon number ranges.

On the other hand, as production of liquid detergents, either heavy- or light-duty, increases, alcohols with shorter carbon chains become important because of their good liquidities and high solubilities. In fact, this tendency has already appeared in some commercial products.

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Table XIX Surface Tension and Critical Micelle Concentration of Disodium Sulfosuccinate Half Ester of C_{12-14}SAE

Surfactant	Surface Tension(dyne/cm)* 0.1%	0.01%	0.001%	C M C wt%	m.mol/kg
SFT-MES-0**	43.2	52.2	61.0	1.0	23
SFT-MES-3	39.0	48.4	60.0	0.20	3.6
SFT-MES-5	39.2	44.6	60.3	0.08	1.5
SFT-MES-7	39.3	45.4	61.1	0.08	1.2
SFT-MES-9	39.6	47.5	61.5	0.15	1.8
SFT-MES-12	40.9	49.0	61.9	0.20	2.1

* : Du Nouy Method, at 25°C
** : EO mole Number

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Table XX Toxicological Properties of Disodium Sulfosuccinate Half Ester of C_{12-14} SAE(SOFTANOL-MES Series)*

No.	Sample	Concentration (% by wt.)	pH (5%)	Irritation(Rabbit)** To Skin	To Eye	LD_{50}(Rat) (ml/kg.day) Male	Female
(1	SFT-MES-3***	20	6.5	A	C-D	17.9	18.6
(2	"	10	6.9	---	B		
(3	"	5	6.9	---	A		
(4	SFT-MES-7	20	6.8	A	B-A	40<	40<
(5	SFT-MES-12	20	6.8	A	A	40<	40<
(6	Lauryl-MES-3	20	6.8	A	C-D		
(7	Oxo-Alc.-MES-3	20	6.8	A	---		
(8	Lauryl-AES-2	20	7.3	C	C-B		
(9	C_{12-14}Sec-AES-3	20	7.2	B	B	15.2	13.7
(10	C_{12}Soap	20	9.8	C	C		
(11	L A S	20	7.7	C	---		
(12	(1 + (8 (1:1)	20	6.6	A	B-A		
(13	(4 + (8 (1:1)	20	6.7	A	A		

* : These data were provided by Y. Yanagimoto (The Life Science Laboratory)
** : Method, by Draize's score. (Assoc. of Food and Drug Officials of the U.S., Austin, TX pp. 46-59(1959)). Irritation Rating : A = None, B = Mild, C = Moderate, D = Severe.
*** : EO mole Number.

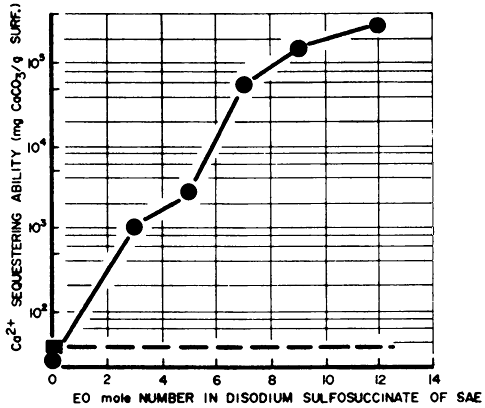

Figure 37. Calcium ion sequestering ability of disodium sulfosuccinate half ester of C_{12-14} secondary alcohol ethoxylates (SFT-MES-series) ((–●–) SFT-MES-series; (–■–) LAS)

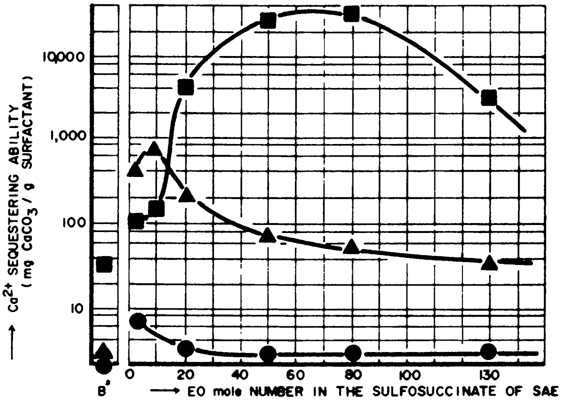

Figure 38. Calcium ion sequestering ability of disodium sulfosuccinate half ester of C_{12-14} SAE (SFT-MES-series) in combination with another anionic. Test conditions: surfactant concentration: SFT-MES-series—0.1 wt %; others—0.1 wt %; B = without SFT-MES-series (blank). ((–●–) with sodium laurate; (–▲–) with SDS; (–■–) with LAS)*

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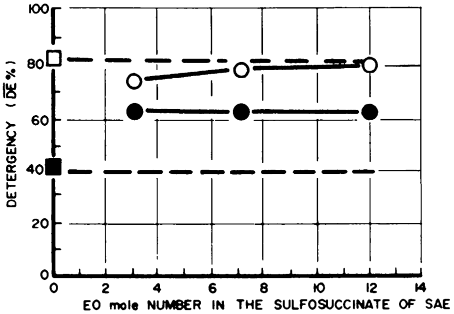

Figure 39. Detergency of disodium sulfosuccinate half ester of $C_{12\text{-}14}$ SAE (SFT-MES-series) with or without builder. Test conditions: surfactant concentration—0.03 wt %; builder concentration—0.12 wt %; cloth—cotton broadcloth; builder composition—shown in Figure 20; other conditions—shown in Table XIV. ((–○–) SFT-MES-series and builder; (–□–) LAS and builder; (–●–) SFT-MES-series alone; (–■–) LAS alone)

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Colin Houston & Associates has recently reported(35) that "Such legislation as the Toxic Substances Control Act, the 1977 amendments to the Clean Water Act, and the Safe Drinking Water Act cloud the future of the more environmentally persistent surfactants containing cyclic rings in their structure, - - - - - Depending on the EPA's implementation of its mandates, the industrial use of surfactants could be altered toward the linear surfactants synthesized from paraffins and alcohols".

Secondary alcohol ethoxylates derived from n-paraffins should, therefore, find wide and long term demand because of their safety and low skin irritation, and the increasing demands for liquid and low foam detergents.

Acknowledgment

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10

Higher Linear Oxo Alcohols Manufacture

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Most synthetic higher alcohol production today utilizes either a variation of the original Oxo technology or the Ziegler technology. This paper presents an example of the Shell process which is a modified Oxo process. This process is very flexible and with associated processes has been developed and utilized by Shell through an integrated package that yields high quality biodegradable detergent materials based on hydrocarbon distillates. This series of processes includes the following:

- Ethylene production via cracking of hydrocarbons from crude oil fractions. This process is in general use.

- Oligomerization of ethylene to higher even carbon number alpha olefins. This is the growth part of the Shell Higher Olefin Process (SHOP) Unit.

- Production of higher olefins from lower and higher linear alpha olefins via isomerization and disproportionation (I/D). This is the detergent olefin production part of the SHOP unit.

- Hydroformylation of the internal olefins from the above processes to alcohols utilizing a proprietary catalyst system. This is the part covered in this paper. It can utilize many possible feed stocks, including those from the SHOP unit.

- Ethoxylation of the alcohols to biodegradable detergent species using ethylene oxide from direct ethylene oxidation. This process is also in wide use.

The processes are flexible and efficient and the alpha olefin products from the SHOP unit can be reacted in either the SHOP I/D unit or in the hydroformylation process depending on which is most desirable. This then avoids the problem of low value byproducts.

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Some aspects of these processes are covered by patents owned by Shell Oil Company (1,2,3).

The original Oxo process (or more accurately, hydroformylation process) is based on reacting a mixture of 1:1 hydrogen and carbon monoxide (synthesis gas) with an olefin to produce an aldehyde one carbon number higher than the olefin. This aldehyde is then converted to the alcohol by hydrogenation after cobalt catalyst removal. Disadvantages of the original Oxo cobalt catalyst system included a requirement of about 200 atmospheres pressure, and that the catalyst be decomposed and redissolved for recycle. Various improvements have been made in this technology by different companies. Shell's catalyst system has five primary advantages over the original Oxo catalyst system. These are:

1. It is quite stable and after crude product separation can be recycled directly to the reactor system. This eliminates the need for the catalyst decomposition and redissolving steps, thus eliminating the associated losses, operating costs, and some capital investment.

2. It rapidly achieves equilibrium isomerization of the double bond and reacts the alpha olefin to alcohol. This allows many feed source possibilities.

3. It has a high hydrogenation activity so that the main product of the reaction system is alcohol, not aldehyde. This assures low make of heavy byproducts and minimizes additional hydrogenation requirements. It also utilizes commercially available 2:1 synthesis gas.

4. It gives a high ratio of linear to iso-alcohol in the product from linear feeds. This provides both desirable detergent properties and rapid biodegradability.

5. It allows operation at lower pressure, which saves both capital investment and operating costs.

There are some precautions necessary in order to maintain good catalyst activity. Since it is a reduced metal ligand complex it is sensitive to oxidation. It also must be kept balanced for good performance and stability. This is achieved by adjusting the makeup of the catalyst components.

Process Scheme

The reaction part of the process is shown schematically in Figure 1. It consists of feeding a mixture of olefin, sythesis gas and recycle (plus makeup) catalyst to a multistage reactor system. The reactor product is cooled, degassed and fed to vacuum evaporators for crude alcohol recovery.

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The crude alcohol is distilled in falling film evaporators. These units are designed to provide very low residence time and also low absolute pressures. This assures low product and catalyst decomposition losses while minimizing alcohol recycle, thereby minimizing alcohol losses to the heavy ends bleed.

The evaporator bottoms can be recycled directly to the reaction system with only a very small bleed required for rejection of catalyst decomposition products and heavy ends. The catalyst is stable under evaporator conditions.

Purification of the crude alcohol takes place in five steps. A schematic drawing is shown in Figure 2. The small amounts of ester formed are reverted with a caustic-treating plus water wash. Distillation in a light ends column removes unreacted olefins, paraffin byproduct, plus other light components present in the crude alcohol. A second distillation is used to remove trace heavy components. Hydrogenation eliminates trace unsaturation, aldehydes, etc. Filtration assures clear, solids free product.

The process scheme is not complicated and yields on olefin feed are good. The major byproduct is paraffin from olefin hydrogenation in the reactor system. However paraffin make is low. Also some olefin remains unconverted, some dimer is formed, and traces of other byproducts are made. These include acetals, esters and diols. These other losses (excluding paraffins) total less than 5%.

The equipment is almost all carbon steel. Some alloy is used, where caustic is present, to minimize the risk of stress cracking.

The paraffins made can be separated and after suitable treatment, recycled to a dehydrogenation unit such as a chlorination - dehydrochlorination unit to reform the olefin. This improves the overall yield.

Product Quality and Uses

The alcohol quality is excellent. The reaction is clean in that minimal byproducts are formed. The chemical cleanups with caustic and later with hydrogen essentially eliminate close boiling impurities. The heart cutting removes light ends and heavy end impurities. The residual hydrocarbons are separated with the light ends, and the dimers and diols with the heavy ends. Typical properties of the alcohol products are good. The alcohol purity is typically above 99%. The products are clear and water white. Acidity, unsaturation and ester content are low. Residual hydrocarbons are typically below 0.3%w. Some branched alcohol is produced but linear olefins yield about 80% linear alcohols. The carbon number distribution of the alcohol will be displaced from the olefin feed distribution by about one carbon number. Olefin feed containing up to three adjacent carbon numbers can be used; more than three carbon numbers make

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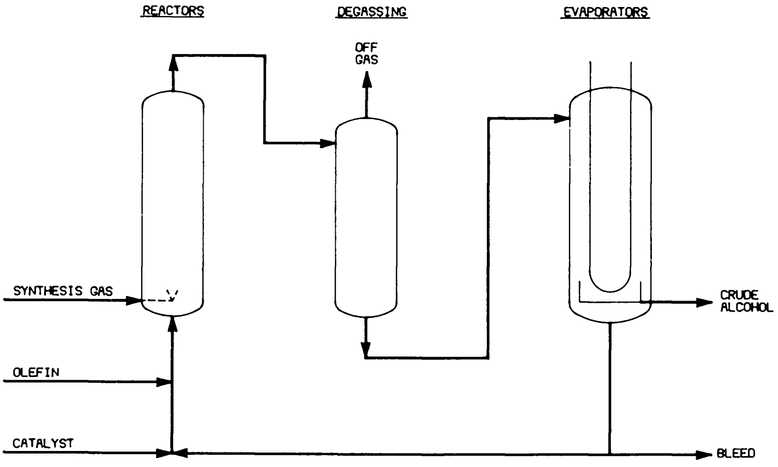

Figure 1. Alcohol reaction and recovery system

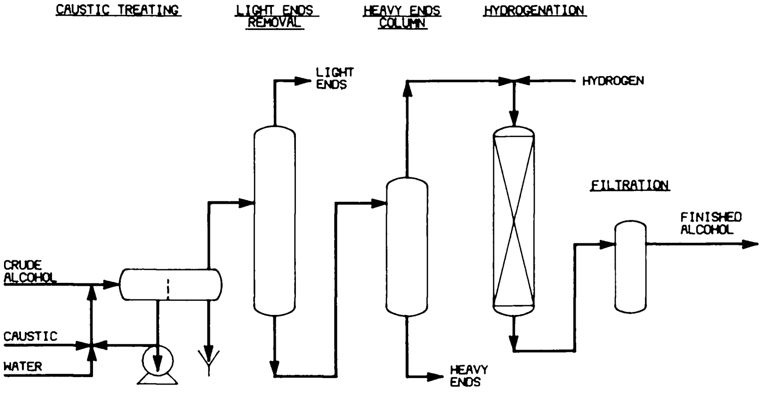

Figure 2. Alcohol purification system

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purification difficult. With narrower ranges, it is possible to switch feeds without emptying the system if the product mix can be used.

These alcohols are readily ethoxylated or sulfated to active biodegradable detergent species. The possible variations in alcohols, their mixtures and the amount of ethylene oxide or sulfation agent used provides a very wide range of possible detergent materials. Many different products are now being produced using this technology.

Feed Sources

Many types of feed have been used successfully in this process. Since the feed is narrow in boiling range and the resulting alcohol is higher boiling, the process is not sensitive to hydrocarbon feed impurities. Wax cracked olefins have been used over both the plasticizer range (C_6 to C_{10}) and the detergent range(C_{11} to C_{15}). Olefins produced by dehydrogenation of paraffins have been used. For example, both Pacol-Olex® olefins and olefins from chlorination-dehydrochlorination are acceptable feeds. The olefins from Shell's Higher Olefin Process (SHOP) are also now providing both plasticizer and detergent range alcohols. Both alpha olefins and internal olefins have been hydroformylated to alcohols. The SHOP process has been described elsewhere (4) and uses ethylene oligomerization plus isomerization and disproportionation to tailor the olefins to the desired carbon number. The ability of the hydroformylation catalyst to handle internal olefins and give essentially the same product as with alpha olefins is especially valuable with this olefin source.

Although the catalyst system produces a high ratio of linear alcohols from linear olefins, the process is not limited to linear olefin feeds. Branched olefins such as butylene dimer and propylene trimer can be used to make iso-alcohols with very little difference in yield. Also the alcohol units are designed to handle different carbon number feeds so that it is possible for a single unit to produce alcohols in the plasticizer range as well as the detergent range. This allows complete flexibility to utilize a wide range of feeds and to produce desired products.

Commercial Utilization

Shell's version of the Oxo process is in use in several foreign countries as well as in the U.S. The first commercial use of this catalyst system was for the production of normal butanol and 2-ethylhexanol in 1963. It is expected to continue to be Shell's primary process for the conversion of olefins to alcohols. This process has produced higher alcohols efficiently since its first commercial application in 1965. This is due to its simplicity, its high quality products and its flexibility to utilize many different feedstocks.

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Synthetic Lubricant Basestocks from Monohydric Alcohols

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With the advent of petroleum shortages, federal Corporate Average Fuel Economy regulations and over $1.00 per gallon gasoline, fuel economy has become the by-word of the automotive industry. As a result, lubrication along with many other automotive parameters has come under technical scrutiny as a route to improved gasoline mileage. This improved fuel economy can be achieved in crankcase oils through reducing the oil viscosity and the inclusion of friction modifiers (slippery agents) (1, 2). However, these changes must be accomplished without negatively affecting the durability or performance of the oil. The viscosity of the oil must be reduced without substantially increasing the volatility of the oil. This can be accomplished by replacing all or part of the broad distillation cut petroleum basestocks which are commonly used with narrow distillation cut synthetic basestock (3, 4). The more economic approach is to use as little synthetic as possible to accomplish your goals. Esters and polyalphaolefins appear to be excellent candidates for such an application.

It should also be mentioned that low oil viscosity at low temperatures is desirable in the new small 4 cylinder and V-6 cylinder fuel economy automobiles (5, 6). This is to permit sufficient speed of engine cranking for cold weather starting at winter temperatures. Low oil volatility must be maintained to prevent oil misting and blowby from poisoning the catalyst system and oxygen sensors in the anti-pollution devices (7).

Ester Manufacture

Most commercially manufactured esters are produced by reacting an alcohol with a carboxylic acid. This esterification reaction is reversible and is commonly referred to as a condensation reaction, since water is a by-product. The type of ester under consideration is referred to as a diester and can be produced by reacting a monohydric alcohol with a dicarboxylic acid. For example:

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$$2\ ROH + HO\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_x\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH \rightleftharpoons RO\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_x\text{-}\overset{\overset{O}{\|}}{C}\text{-}OR + 2H_2O$$

Monohydric Alcohol + Dicarboxylic Acid $\rightleftharpoons$ Diester + Water

Typical raw materials used to manufacture low volatility diesters are found in Table I. An alternate route to the diesters is to start with the methyl ester of the dibasic acid and arrive at the diester via alcoholysis reaction. In this case, methanol is the co-product.

Since esterification is an equilibrium reaction, most commercial manufacturing methods generally require heating the reactants with an excess of the alcohol - the more volatile reactant. This helps drive the equilibrium in the direction of the ester product. Water of reaction is removed either by azeotroping with a special agent such as xylene or by vacuum distillation and stripping. The reaction progress is followed by measuring acidity (8). The crude ester can be refined by various methods to improve quality. For example, the ester can be treated with sodium carbonate to neutralize trace acidity (9).

Basestock Property Study

As evidenced in Table II and Figure 1, the monohydric alcohol used in making the diester has a very pronounced effect on low temperature and volatility characteristics. For comparison purposes, both petroleum and polyalphaolefin (PAO) basestocks are included in the data. The data indicate that increased branching of the alcohol has the following effects on the resulting diester:

1. Improved low temperature properties
2. Increased volatility

Increasing the molecular weight of the monomeric alcohol results in the following trends in the diester:

1. Higher viscosity
2. Lower volatility

The ideal diester for use in a partial synthetic lubricant, i.e. blend of diester, petroleum basestock and additives, should have the lowest viscosity at both high and low temperatures, and also be the least volatile. Of course, it would also need to be resistant to oxidation and corrosion and provide lubrication and wear protection when compounded into a finished lubricant. The low viscosity requirement of the synthetic portion of the partial synthetic lubricant is for economic reasons. The synthetic portion is substantially more expensive than the petroleum portion and the lower the amount required to achieve the low viscosity of the final oil, the better the final economics. As mentioned earlier, the low volatility is desirable to prevent carrying the

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TABLE I

Raw Materials for Diesters

Monohydric Alcohols

No. of Carbons	Name
8	2-ethylhexyl alcohol
8	isooctyl alcohol
10	isodecyl alcohol
13	isotridecyl alcohol

Dibasic Acids

No. of Carbons	Name
6	adipic acid
9	azelaic acid
10	sebacic acid
8	phthalic anhydride

TABLE II

Basestock Properties

	Viscosity[a] 210°F	0°F	-65°F	Pour Point, °F ASTM D 97
di-n-octyl azelate DNOZ	3.3	Solid	Solid	+40
di-2-ethylhexyl azelate DEHZ	3.0	256	6400	-100
di-isooctyl adipate DIOA	2.4	217	5314	< -80
di-n-decyl azelate DNDZ	4.2	Solid	Solid	+75
di-isodecyl azelate DIDZ	4.3	400	24000	-95
di-isotridecyl azelate DITZ	6.6	1070	18700 (-40°F)	-70
polyalphaolefin, 6 cSt PAO-6	6.1	635	53000	-90
polyalphaolefin, 4 cSt PAO-4	4.0	347	14000	-100
100N petroleum	3.0	545	Solid	0
200N petroleum	4.4	1800	Solid	0

a ASTM D 445 for 210°F viscosity (cSt)

ASTM D 2602 for 0°F viscosity (cP)

ASTM D 2532 for -65°F viscosity (cSt)

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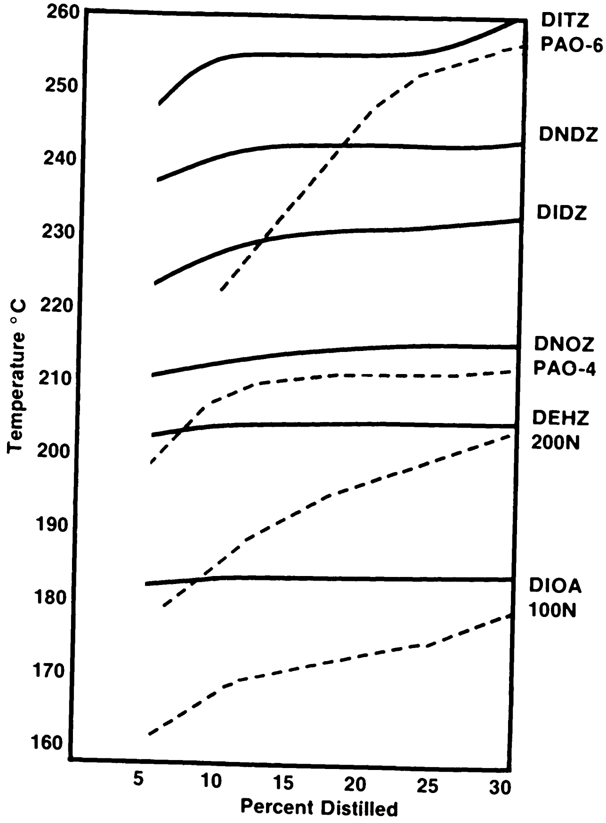

Figure 1. ASTM D 1160 distillation (1 mm Hg)

phosphorus-containing additive to the catalyst and oxygen sensor in the anti-pollution devices and causing their premature failure through chemical poisoning (7).

Table II and Figure 1 data show di-2-ethylhexyl azelate (DEHZ) has excellent low viscosity at low temperature along with good volatility properties. Figure 1 shows the DEHZ to have substantially lower volatility than DIOA and actually lower volatility than 4 cSt polyalphaolefin (PAO-4) in the initial distilled loss area of the curves. The slopes of the PAO and petroleum curves in Figure 1 indicate they are composed of a distribution of different molecular weight species, whereas the relatively flat curves of the esters indicate they are essentially composed of a single chemical species. As a result, there are little or no low molecular weight ends to increase the volatility of these diesters. Even though the PAO is a very narrow distillation cut, it is still composed of a blend of dimers, trimers, tetramers, and pentamers, and does exhibit volatility caused by the low ends as demonstrated in Figure 1.

Compounded Lubricant Study

It was decided to blend some of the diesters at 15% weight level into a prototype 5W-30 partial synthetic automotive crankcase formulation. The 15% level was arbitrarily assigned for economic reasons. The 0°F and 210°F viscosities were run on each formulation to define if it met 5W-30 viscosity requirements. Current SAE viscosity classifications require that a 5W-30 cross grade oil formulation exhibits a 9.6 to 12.9 cSt viscosity at 210°F and 1200 max. cP at 0°F. The latter test is referred to as a cold crank simulator test and it is supposed to correlate with low temperature cranking of an automobile engine. See Table IV for a description of the current SAE Viscosity Classification requirements. It is seen in Table III that only DEHZ, DIOA, and PAO-4 meet the 5W-30 viscosity requirements in this formulation, with the DEHZ and DIOA esters being more efficient (lower viscosity) than the 4 cSt PAO. This latter statement was confirmed by comparing the viscosity effect of different levels of DEHZ, PAO-4, and PAO-6 in 100N petroleum oil at 210°F and 0°F. The results are shown in Figures 2 and 3. In both cases, the DEHZ exhibits a superior degree of dilution efficiency.

A new proposed SAE Viscosity Classification not only reflects lower than 0°F temperature cranking characteristics of an oil, but also covers low temperature pumpability characteristics (6, 10). Low temperature cranking success without oil pumpability could result in oil starvation and subsequent engine damage. This new proposed classification attempts to establish a maximum cranking viscosity and then classifies oils according to what temperature they match this viscosity. It also includes a low shear test (mini-rotor viscometer) to duplicate pumpability of the oil at various low temperatures. Needless to say, minimum

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TABLE III

Synthetic Basestock Study

	Weight Percent						SAE Viscosity Classifications	
	A	B	C	D	E	F	5W	30
PMA-VI Improver	6.65	6.65	6.65	6.65	6.65	6.65		
Additives	9.10	9.10	9.10	9.10	9.10	9.10		
100SN	69.25	69.25	69.25	69.25	69.25	84.25		
DEHZ	15.00	-	-	-	-	-		
DIDA	-	15.00	-	-	-	-		
DIOA	-	-	15.00	-	-	-		
PAO-4	-	-	-	15.00	-	-		
PAO-6	-	-	-	-	15.00	-		
Vis. 0°F,cP	1082	1226	1054	1142	1294	1400	1200 max.	
Vis. 210°F, cSt	9.7	10.2	9.7	9.7	10.4	10.1		9.6-12.9
SAE 5W-30 Grade	Yes	No	Yes	Yes	No	No		

TABLE IV

SAE Viscosity Classifications

SAE Viscosity Number	Viscosity Units	At 0°F (-18°C) min.	At 0°F (-18°C) max.	At 210°F (99°C) min.	At 210°F (99°C) max.
5W	Centipoises	-	1,200	-	-
	Centistokes	-	1,300	-	-
	SUS	-	6,000	-	-
10W	Centipoises	1,200	2,400	-	-
	Centistokes	1,300	2,600	-	-
	SUS	6,000	12,000	-	-
15W	Centipoises	2,400	4,800	-	-
	Centistokes	2,600	5,200	-	-
	SUS	12,000	24,000	-	-
20W	Centipoises	2,400	9,600	-	-
	Centistokes	2,600	10,500	-	-
	SUS	12,000	48,000	-	-
75W	Centipoises	150,000	@ -40°F (-40°C)	4.2 cSt	-
	SUS	-	-	40	-
80W	Centipoises	150,000	@ -15°F (-26°C)	7.0 cSt	-
	SUS	-	-	49	-
20	Centistokes	-	-	5.7	9.6
	SUS	-	-	45	58
30	Centistokes	-	-	9.6	12.9
	SUS	-	-	58	70

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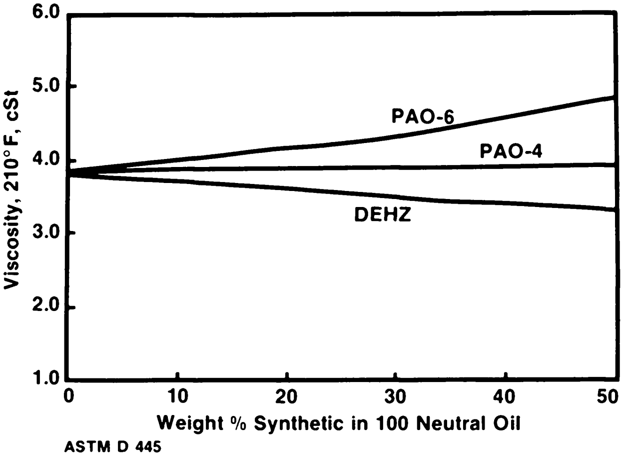

*Figure 2. Synthetic basestock blends with 100*N *petroleum oil*

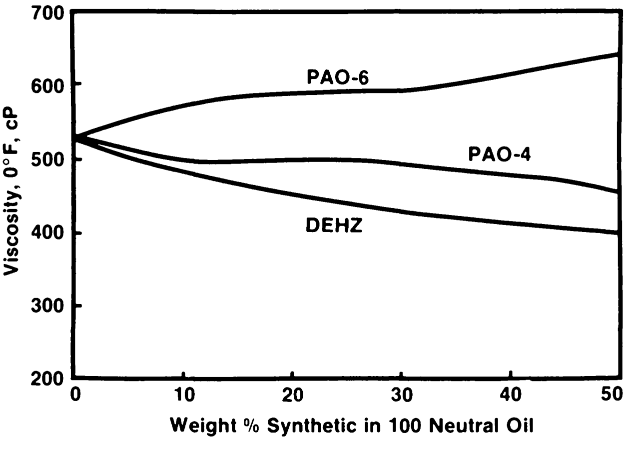

*Figure 3. Synthetic basestock blends with 100*N *petroleum oil*

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pumpability temperature should be lower than minimum crankability temperature. These new proposed viscosity classifications are presented in Table V. A quick review of the -65°F viscosities and pour points in Table II will indicate that the new proposed viscosity classification chart favors the use of synthetics as viscosities below 0°F become critical.

Engine Testing

Through the cooperative efforts of SAE, ASTM, and API, passenger car engine oil classifications are established. These describe certain stationary engine tests which all oils must pass before being acceptable for use in the modern day automobile engine. These requirements are continually changing as engines become more and more difficult to lubricate. Table VI describes some of the requirements and the transition of test requirements from classifications SE to SF. The various tests are designed to test bearing wear and viscosity loss (L-38), rust (II-D), sludge and varnish (III-D and V-D), and wear (III-D and VD) of the oil. The DEHZ basestock was selected as an efficient compromise for desired properties in a partial synthetic oil. An engine oil was formulated using 200 neutral oil, 100 neutral oil, polymethylmethacrylate viscosity index improver, an additive package, and 15% DEHZ. See Table VII under Current 5W-30. This 5W-30 formulation was then subjected to the various tests described in Table VI for qualification as an SF engine oil. The results are presented in Table VIII.

As can be seen, this partial synthetic passenger car crankcase lubricant based upon the 2-ethylhexanol diester of azelaic acid very successfully passed the engine tests required to qualify as an SF grade engine oil. All of these tests were successful on the first try. It is not unusual for multiple runs to be made before a pass is obtained.

On the III-D test, the 5W-30 partial synthetic showed better resistance to viscosity increase than typical petroleum based oils. All petroleum reference oils ran from 851% to 3077% on viscosity increase after 64 hours. These were straight 30 weights and 10W-30 viscosity oils as opposed to the partial synthetic being a 5W-30 oil. Visual observation showed no scuffing of rocker arm pivots on the first III-D test in Table VIII. Wear was observed on seven of the rocker arm pivots. A second III-D test was run on the slightly higher viscosity version shown under Proposed 5W-30 in Table VII. It demonstrated excellent cam and lifter wear with no wear or scuffing visible on any of the rocker arm pivots. See Table VIII. The oil consumption of this formula ran 4.97 quarts versus 5.59 quarts and 5.72 quarts for the 10W-30 all petroleum oil reference data supplied with the test.

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TABLE V

Proposed SAE Low-Temperature Engine Oil Viscosity Classification

Proposed Grade	Maximum Viscosity, cP, at Temperature, °C ASTM D 2602	Maximum Viscosity (300P) and Yield Stress (105Pa) at Temperature, °C a	Minimum Viscosity cSt, at 100°C ASTM D 445
0W	3250 at -30	-35	3.8
5W	3500 at -25	-30	3.8
10W	3500 at -20	-25	4.1
15W	3500 at -15	-20	4.1
20W	4500 at -10	-15	5.6
25W	6000 at -5	-10	9.3

a ASTM Method not Finalized

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TABLE VI

Current API Passenger Car Engine Oil Classification

Test	SE	SF
II-C, rust, min. rating	8.4	-
II-D, rust, min. rating	8.5	8.5
III-C		
Sludge, min. rating	9.2	-
Piston Varnish, min. rating	9.1	-
Ring Land Varnish, min. rating	6.0	-
Wear-(Cam + Lifter)-avg.	0.0040"[a]	-
-max.	0.0100"[a]	-
Viscosity Increase % @ 40°C, max.	375 @ 40 hrs.	-
III-D		
Sludge, min. rating	9.2	9.2
Piston Varnish, min. rating	9.1	9.2
Ring Land Varnish, min. rating	4.0	4.8
Wear-(Cam + Lifter)-avg.	0.0040" max.	0.0040" max.
-max.	0.0100"	0.0080"
Viscosity Increase % @ 40°C, max.	375 @ 40 hrs.	375 @ 64 hrs.

[a]Recommended, not a required limit

Test	SE	SF
V-C		
Sludge, min. rating	8.7	-
Piston Skirt Varnish, min. rating	7.9	-
Average Varnish, min. rating	8.0	-
Oil Ring Clogging, %, max.	5 max.	-
Oil Screen Clogging, %, max.	5 max.	-
Compression Ring Sticking	None	-
V-D (9-L)		
Sludge, min. rating	8.5[b]	9.4
Piston Skirt Varnish, min. rating	6.7[b]	6.6
Average Varnish, min. rating	6.3[b]	6.7
Wear-(Camshaft)-avg.	Rate & Report[b]	0.0010"
-max.	Rate & Report[b]	0.0025"

[b]Proposed as alternate to V-C limits

Test	SE	SF
L-38		
Bearing Wt. Loss, mg., max.	40	40
Piston Varnish, min. rating	-	9.0

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TABLE VII

Composition and Laboratory Test Data
On 5W-30 Partial Synthetic Motor Oils

Composition	Weight %	
Ingredients	Current 5W-30	Proposed 5W-30
100 Neutral Oil	57.25	27.25
200 Neutral Oil	12.00	42.00
PMA-VI Improver	6.65	6.65
DEHZ	15.00	15.00
Additives	9.10	9.10
Tests		
Specific Gravity	0.886	0.886
Pounds per gallon	7.38	7.38
Viscosity, cSt, 210°F	10.3	11.0
Viscosity, cSt, 100°F	57.3	62.8
Viscosity, cP, Cold Crank Simulator, 0°F	1119	1450
Viscosity Index	182	180
Flash Pt., COC, °F	415	415
Fire Pt., COC, °F	445	445
Pour Pt., °F	-30	-30
Total Base Number	1.9	1.9

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TABLE VIII

Engine Test Data on 5W-30
Partial Synthetic Motor Oil

Test	Results	SE	SF
II-D, Rust	8.89	8.5 min.	8.5 min.
III-D (current 5W-30 visc.)			
Sludge	9.54	9.2 min.	9.2 min.
Piston Varnish	9.44	9.1 min.	9.2 min.
Ring Land Varnish	7.12	4.0 min.	4.8 min.
Wear- (Cam + Lifter)-avg.	0.0039"	0.0040" max.[a]	0.0040" max.
-max.	0.0046"	0.0100"[a]	0.0080"
Viscosity Increase (% at 40°C)	99 @ 40 hrs. 136 @ 64 hrs.	375 max. @ 40 hrs.	375 max. @ 64 hrs.
Oil Consumption	5.63 Qts.	-	-
III-D (proposed 5W-30 visc.)			
Sludge	9.2	9.2 min.	9.2 min.
Piston Varnish	9.15	9.1 min.	9.2 min.
Ring Land Varnish	6.60	4.0 min.	4.8 min.
Wear (Cam + Lifter)-avg.	0.0026"	0.0040" max.[a]	0.0040" max.
-max.	0.0037"	0.0100"[a]	0.0080"
Viscosity Increase (% at 40°C)	59 @ 40 hrs. 98 @ 64 hrs.	375 max. @ 40 hrs.	375 max. @ 64 hrs.
Oil Consumption	4.97 Qts.	-	-

[a]Recommended, not a required limit

Test	Results	SE	SF
V-D (9-L)			
Sludge	9.41	8.5 min.[b]	9.4 min.
Piston Varnish	8.10	6.7 min.[b]	6.6 min.
Average Varnish	7.92	6.3 min.[b]	6.7 min.
Wear-(Camshaft)-avg.	.0005"	Rate & Report[b]	0.0010" max.
-max.	.0008"	Rate & Report[b]	0.0025"
Oil Ring Clogging, %	0		
Oil Screen Clogging, %	0		
Compression Ring Sticking	0		

[b]Proposed as alternate to V-C limits

Test	Results	SE	SF
L-38			
Bearing Wt. Loss, mg.	21.9	40 max.	40 max.
Piston Varnish	9.6	-	9.0 min.

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Conclusions

Diesters prepared from specific monohydric alcohols can be formulated into low viscosity partial synthetic automotive crankcase lubricants. These diester basestocks exhibit definite advantages over petroleum basestocks of similar and sometimes higher viscosities. These advantages are:

1. Much lower volatility at equal or lower viscosity at 210°F as demonstrated by comparing DEHZ with 100N and 200N petroleum oils.
2. Much improved low temperature properties at comparable 210°F viscosity as demonstrated by comparing DIDZ with 200N oil.

The diesters also show some advantage over PAO's in viscosity dilution efficiency as shown in Table III where DEHZ and DIOA gave lower 0°F viscosities than PAO-4. Figures 2 and 3 also demonstrate this advantage when DEHZ is compared to PAO-4 and PAO-6 in viscosity dilution effects.

The actual engine test data shown in Table VIII indicate that diester based 5W-30 partial synthetic oil can very successfully pass the requirements for SE/SF qualification while showing oil consumption rates better than 100% petroleum 10W-30 oils.

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Monohydric Alcohol Ester Plasticizers for Polyvinyl Chloride

Past, Present, and Future

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As noted in the Preface, monohydric alcohols are generally categorized as lower (C_1-C_5) and higher (C_{6+}) alcohols. The largest outlet by far for higher monohydric alcohols is in ester type plasticizers for polyvinyl chloride (PVC). The PVC plasticizer range alcohols are generally considered to be C_6-C_{11}, although branched chain tridecyl alcohol is also of importance. Of the lower alcohols, only normal butanol, and to a far lesser extent isobutanol, are used in this application. Total volume of these lower alcohols used is small by comparison.

The Decade of the Thirties - The Beginning

The use of monohydric alcohol esters as PVC plasticizers had its beginning in the decade of the thirties. Plasticization of PVC was first demonstrated by W. D. Semon of B. F. Goodrich(1). Semon's patent gave examples of plasticizers such as dibutyl phthalate and other unrelated compounds. However, the claims were limited to non specific aromatic substances, liquid aromatic nitro compounds, and specific aromatic nitro compounds. The first commercially used plasticizers for PVC were those already available and used as cellulosic plasticizers, such as the monohydric alcohol ester--dibutyl phthalate.

Di-2-ethylhexyl phthalate (DOP) had already been patented as a composition of matter and examples of its use as a plasticizer for cellulosics, etc., but not PVC, were cited(2). However, it was not until later in the decade that the overall advantages of DOP were recognized. This was a key factor in the large scale production of 2-ethylhexanol (2EH) by Union Carbide Corp. starting in 1939(3), followed shortly by the commercialization of DOP -- also by Union Carbide(4). 2-Ethylhexanol was made at that time via the "double aldol" route, starting with acetaldehyde.

It is interesting to note that DOP showed no particular virtue as a plasticizer for the other resins available at the time. Were it not for flexible PVC, DOP might have passed into obscurity(3). Instead, as is well known, DOP became the industry

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standard for PVC and is still the single largest volume plasticizer produced to this day, on a worldwide basis.

The Decade of the Forties - Flexible PVC Takes Off

During the early forties flexible PVC use was mainly limited to military applications, including wire and cable, and various film and sheeting applications, etc. With the conclusion of World War II, new markets for PVC developed rapidly. Aside from DOP, which was commercialized in 1940(4), dicapryl phthalate (DCP) was introduced by Rohm and Haas(5), also in the early forties. With the development of plastisols(6), DCP became a plasticizer of choice because of the favorable balance of properties it imparted -- especially low viscosity. However, DCP's subsequent growth has been limited since capryl alcohol (octanol-2), a monohydric secondary alcohol, is a by-product of limited volume sebacic acid manufacture.

It is noteworthy that the only monohydric secondary alcohols that have found any use in PVC plasticizers are capryl alcohol (octanol-2) and cyclohexanol. No tertiary alcohols have found use at all, probably because of the difficulty of esterification, at least.

Other 2-ethylhexanol based plasticizers were introduced, including some which imparted outstanding low temperature flexibility--dioctyl adipate (DOA), dioctyl azelate (DOZ), dioctyl sebacate (DOS), and trioctyl phosphate (TOF). In addition, TOF showed high resistance to microorganisms which was important in military applications. Furthermore, TOF improved flame resistance. However, the mixed ester--octyl diphenyl phosphate--also introduced in the forties--was far superior and showed a better balance of low temperature performance and flame resistance than either TOF or the well-established plasticizer--tricresyl phosphate (TCP). Each of these found a market as a specialty plasticizer because of these specific performance attributes. None, however, was a serious threat to DOP on an overall price-performance basis. Rather, they were used to supplement the properties of DOP where its performance was inadequate.

Meanwhile, Rohm and Haas introduced the first of the polymerics - polyesters based on the reaction of a dibasic acid with a glycol and with a monohydric alcohol or monobasic acid as chain terminator(5). These plasticizers were developed as highly permanent, extraction and migration resistant types for specialty applications. 2-Ethylhexanol and isodecyl alcohol are examples of monohydric alcohols used as chain terminators in today's polymerics.

The oxo process, discovered in Germany by Otto Roelen, was a breakthrough method of producing primary monohydric alcohols. The oxo process was commercialized by Exxon Chemical Co. in the U.S. in 1948 with the manufacture of isooctyl alcohol(7). This

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quickly led to the introduction of diisooctyl phthalate and other ester-type plasticizers similar to those based on 2-ethylhexanol.

Still in the forties, butyl benzyl phthalate (BBP) was introduced by Monsanto Co. This ester is based on the monohydric alcohol n-butanol, but the benzyl group is derived from benzyl chloride rather then benzyl alcohol. This route was selected to make possible manufacture of pure coester which showed a better balance of properties than if made from the two alcohols. BBP was destined to make its mark in PVC, particularly in the flooring industry.

Aside from the plasticizers mentioned, there was feverish activity to develop other basically new types by a host of companies. About twenty thousand plasticizers were mentioned in the literature by 1943(8). Certainly hundreds of candidate plasticizers were actually sampled by the industry during the period 1945-1955. Most, however, failed to show an advantageous balance of performance and price when compared to already existing products.

The Decade of the Fifties - The Oxo Process Exploited

During the fifties there was widespread activity in the oxo process area. Additional branched chain primary monohydric alcohols - isodecyl and tridecyl - were introduced by Exxon Chemical Company. The phthalates of these alcohols were found to be particularly useful in high temperature PVC insulated wire and cable where DTDP, for example, partially replaced the more costly polymerics(9).

Meanwhile, lower monohydric alcohols were first made by the oxo process. These included n-propanol, n- and isobutanol and amyl alcohol. In PVC, only one of these assumed any importance - n-butanol - mainly in butyl benzyl phthalate. Dibutyl phthalate (DBP) was by this time considered too volatile for use in PVC in the U.S.(10). The so-called coesters - butyl octyl phthalate (BOP), butyl isodecyl phthalate and butyl cyclohexyl phthalate - have been on and off the market for many years but never achieved major success in the U.S. Dibutyl phthalate/DOP blends and BOP have probably been most successful in Japan. Diisobutyl phthalate is used in Brazil and other South American countries even today, because of its low cost. BOP is also offered in Europe, but as in the U.S., it has not been a major success. One reason could be the wide variability of composition from different suppliers. In fact, some BOP's were merely physical blends of DBP and DOP.

While n-butanol from the oxo process did not become a major intermediate for PVC plasticizers, the development was nonetheless a breakthrough of far-reaching significance. The precursor of n-butanol in the oxo process is n-butyraldehyde. This made possible the manufacture of 2-ethylhexanol by "single aldol" at lower cost than the "double aldol" route via acetaldehyde.

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The commercialization of isophthalic acid by Chevron in 1956(11) led to the introduction of di-2-ethylhexyl isophthalate (DOIP). This plasticizer showed improved lacquer mar resistance in flexible PVC(12). This need was limited, however. Because of its premium price, DOIP has not gained acceptance as a general purpose plasticizer.

Following the successful development of epoxidized soybean oil(5), mainly as a stabilizer adjuvant with high permanence but poor low temperature plasticizing properties, the epoxidized fatty acid esters were introduced. These included the C_8 monohydric alcohol esters -- octyl epoxystearate and octyl epoxytallate. They also acted as stabilizer adjuvants but with outstanding low temperature plasticizing properties. The epoxy stabilizer/plasticizers have grown to over 50,000 tons/year in the U.S. in 1978, with the epoxidized soybean oil type predominating.

The Decade of the Sixties - The Straight Chain/Linears Emerge

Hexyl alcohol, a mixture of n- and iso C_6 alcohols made via the oxo process by Exxon Chemical Co., started the flow of new monohydric alcohols as intermediates for PVC plasticizers in the sixties. Dihexyl phthalate - the phthalate of this alcohol - is a fast solvator and competes with other fast solvating types in markets such as vinyl flooring and carpet backing.

The commercialization of the Ziegler process by Conoco and Ethyl (See Chapter 7) was the next breakthrough in monohydric alcohols production. These straight-chain alcohols are derived from ethylene growth on triethyl aluminum, producing a range of even number primary monohydric alcohols. Phthalates of blends of n-C_6-C_8-C_{10} and n-C_8-C_{10} are known as 610P and 810P, respectively. Their lower volatility and improved economics resulted in a takeover from DOP/dioctyl adipate and similar blends. This was especially important in the automotive upholstery market where important requirements are low temperature flexibility and low fogging - i.e., plasticizers that resist vaporization from vinyl with subsequent condensation on the windshield. Actually, the straight chain ester - di-n-octyl phthalate - was available in the forties. However, n-octanol was produced from coconut oil and was not economically attractive at that time.

Another important development in the early sixties was the commercialization of trimellitic anhydride (TMA). Monohydric alcohol triesters of TMA were shown to have outstandingly low volatility while overcoming the poor low temperature properties of polymeric-type plasticizers. In addition, the TMA esters were lower in cost than the polymerics - particularly when volume cost was considered.

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By the middle of the decade plasticizer production had passed the billion pound level(13), and reached 1.2 billion pounds in 1968, more than fulfilling a prediction made in 1955 by Skeist(14). More than 80% of this production was for PVC.

The next development in plasticizer range monohydric alcohols in the sixties was isononyl alcohol. This branched chain oxo alcohol and its ester (DINP) were commercialized in 1968 by Exxon Chemical Co. DINP offered better overall performance than DOP for most uses, as well as significant compound volume cost advantages. As a result, it has grown rapidly in the marketplace as a general purpose (GP) plasticizer.

As the decade ended, a new monohydric alcohol phthalate based on mixed C_7-C_9-C_{11} straight chain and single methyl branched alcohols was introduced by Monsanto Co. The alcohols are produced by the oxo process from straight chain alpha olefins. The phthalate competed directly with 610P, especially in the automotive upholstery market where it gained rapid acceptance. The term "linear" has been adopted to describe largely straight-chain alcohols(15). In fact, "linear" has come to mean straight chain or largely straight chain, particularly when describing phthalates.

The Decade of the Seventies - From Excess Capacity to Shortages

As the seventies got underway, the premium price on the GP linear phthalates decreased to where these plasticizers also began to capture a share of the general purpose plasticizer market, particularly if improved low temperature flexibility was important. The phthalate of the C_{11} fraction of the linear C_7-C_9-C_{11} alcohols was introduced by Monsanto and found acceptance in high temperature wire and cable where it competes with branched chain DTDP. In Europe, linear alcohol phthalates based on alcohol blends made by oxonation of cracked wax olefins gained acceptance. These differed from the U.S. linear alcohol blends in having both odd and even carbon chain lengths.

The next breakthrough of importance for future 2-ethylhexanol plants occurred in the mid seventies. This was the development of the rhodium-catalyzed oxo process by Union Carbide, Davy Powergas and Johnson-Matthey (See Chapter 6). This process not only operates at lower temperatures and pressures than the conventional cobalt-catalyzed process but also gives a far lower yield of the less valuable isobutyraldehyde by-product. The net result is improved economics vs. the cobalt process for n-butyraldehyde - the intermediate for 2-ethylhexanol. Although outside the U.S. this new technology has already been licensed and plants are now operating(16), no new plants were constructed in the U.S. specifically for 2EH manufacture in the seventies. However, Union Carbide plants in Texas and Puerto Rico have been modified, utilizing this new technology for propionaldehyde and butyralde-

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hyde manufacture, respectively. Some of the latter is believed to be used to make 2EH.

Also in the mid seventies, a new type plasticizer - dioctyl terephthalate (DOTP) - was introduced by Eastman. DOTP is less volatile and has better low temperature flexibility than DOP, although it is less solvating than DOP or even DIDP. A branched chain C_9 terephthalate is reported to be compatible with PVC but not a 70% linear C_9 average phthalate. Most C_6 and lower terephthalates are reported to be incompatible solids(17).

Throughout the history of flexible PVC there have been periods where plasticizers were alternately in a long or short position. Looking back, the seventies was a particularly rough period in this respect for the industry. At the beginning of the decade the market was grossly oversupplied in terms of both alcohol and ester capacity. This condition led to poor profitability and ultimately a restructuring of the marketplace. Many small producers not basic in alcohols and phthalic anhydride dropped out. One major plasticizer supplier left the GP plasticizer market; another left the plasticizer market entirely, and late in the decade a third supplier shut down its 2-ethylhexanol plant due to lack of propylene feedstock. The decade ended with a tight supply situation on plasticizer range monohydric alcohols due largely to the shutdown of the major 2EH plant. Startup of Exxon Chemical's 50% expansion in oxo alcohol capacity helped ease what could have been a major shortage.

The Decade of the Eighties - Slower Growth Seems Probable

At the start of the eighties the plasticizer alcohol supply situation continued tight. However, by the end of the first quarter of 1980 there was a sharp drop in demand which is expected to slowly rise to 1979 levels by about 1983. Projections are for an average growth rate of about three percent for the rest of the decade. This is largely the result of projected reduced demand in both automotive and housing - key indicators for the flexible vinyl industry. There are some new uses emerging, such as vinyl roofing for industrial buildings and automotive undercoatings - both long established in Europe - but there are also inroads on vinyl, for example, in upholstery, wire and cable, and shoes.

New alcohol capacity has been announced by Monsanto Co.(18), and a new joint venture on 2EH by Tenneco Chemicals and USS Chemicals is reported to be approved(19). This new capacity is not due on stream before 1982-1983, however. Also, restart of the former Oxochem 2EH plant in Puerto Rico has been rumored, but no definitive announcement has been made.

Phthalates of C_8-C_{10} average carbon number monohydric alcohols continue to dominate the PVC plasticizer market, and the likely scenario is for this to continue through the eighties. There have been, however, numerous developments which will

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influence the relative importance of the specific monohydric alcohols which will be used. Most of these involve economics - of feedstocks, alcohol processes, and vinyl compounding and fabrication. The remainder involve new or more restrictive end use requirements. Some of these key developments are as follows:

1. The Changing Value of Olefin Feedstocks for Alcohols. Lower olefins - ethylene and propylene - are the basic feedstocks for all important monohydric alcohols used in PVC plasticizer manufacture in the U.S. Thus, the relative values of these olefins are of key importance to manufacturing cost.

While the eighties started with a very tight supply situation on propylene, availability is not now a problem. Longer range, the continuing trend to naphtha and gas oil as cracker feeds in a market that is basically ethylene driven will mean increased amounts of propylene relative to ethylene will be produced. This is expected directionally to increase the historical price differential between ethylene and propylene. In addition, butylenes, which were of relatively minor importance to higher alcohols production in the seventies, will assume increasing importance in the eighties based on announced plans of Monsanto(18). Also, in Japan a new DINP based on Dimersol® octenes from n-butenes is slated for commercialization in 1980-1981(20).

Another factor which will bear on the relative values of these olefins is the burgeoning demand for isobutylene for methyl t-butyl ether as a gasoline octane improver(21). Large amounts of n-butenes will become available which in the past could be utilized as dehydro feed for butadiene. This outlet for n-butenes, however, is declining due to increasing amounts of butadiene from steam crackers. Although new outlets for n-butenes such as polyethylene copolymers are expected to grow, this will not balance the loss of the dehydro feed outlet. The value of n-butenes will continue to be governed by fuel products outlets and could be low compared to ethylene and propylene.

In view of the foregoing, it suffices to say that the relative economics of producing the various plasticizer range monohydric alcohols will be different in the eighties than in the seventies.

2. The Declining Market for Linear Phthalates in Automotive Upholstery. The major market for linear phthalates has historically been automotive upholstery. However, the U.S. built share of the automotive market has continued to decline, and the trend (now a landslide) to smaller cars has resulted in a sharp decrease in demand for domestic vinyl upholstery. Besides this, fashion trends have turned to increased use of non-vinyl upholstery. Finally, the use of softer vinyls with higher plasticizer levels means increased opportunities in the automotive upholstery market for diisodecyl phthalate (DIDP). DIDP meets the low temperature requirements of these new softer vinyls, and at the same time offers reduced windshield fogging and lower cost on a

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compound volume basis than the GP linear phthalates. The lower cost results from DIDP's lower efficiency and specific gravity vs. these standard linear phthalates. The net result is that the linear phthalates are likely to decline in relative importance in the eighties.

3. The Increasing Acceptance of Plasticizers with Better Cost-Performance than DOP. While the breakthrough n-butyraldehyde technology of the mid seventies will tend to make new 2EH capacity competitive with existing plasticizer range alcohol plants, there has been a trend away from DOP in the U.S. Reasons for this include -

- o The fogging problem in automotive interior applications.
- o New or more demanding applications beyond the capabilities of DOP, such as industrial vinyl roofing, and the trend to thinner wall wire insulation and jacketing.
- o The decline in 2EH capacity has, of course, not helped DOP usage. The 2EH supply situation is expected to be corrected in the next few years, as noted earlier. However, during the period when DOP was in short supply many users converted to DINP, DIDP, and linear phthalates. They have found the better overall performance, and in many cases better compound economics of these plasticizers justifies continued use. Although DOP will regain some of its lost ground, it is not expected to dominate the U.S. market as in the past.

4. The Increasing Cost of Energy. Much attention has been given in the literature to the use of various highly aromatic ester-type fast solvating plasticizers as a means of reducing energy requirements and/or increasing plant output. There are certainly some vinyl fabrication operations where this applies. However, increased raw material costs due to the higher cost per pound of most of these fast solvating plasticizers and their high specific gravities (typically 1.12-1.13) must be weighed against possible energy savings. A new non-premium, fast-solvating plasticizer - diisoheptyl phthalate (Jayflex® 77) - was recently introduced by Exxon Chemical Co. This plasticizer overcomes the high specific gravity and poor low temperature performance of the highly aromatic fast solvating type plasticizers. Similar esters have been available in Europe and Japan for many years and have achieved some importance in the latter country.

The specific gravity difference between DOP and a typical highly aromatic fast solvator represents a volume difference of almost 14 percent for the same weight. An example of how this high specific gravity increases raw material cost is shown in Table I. It is apparent that replacing 20% of the DOP in this formulation with a fast-solvating plasticizer has increased the raw material cost of a 100 yard roll of 54 inch width 12 mil sheeting by $0.64. Typical energy costs for a one and one half meter width calender producing 12 mil average thickness sheeting are estimated at 2¢ per pound of compound(22). This includes

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TABLE I

AFFECT OF HIGHLY AROMATIC FAST SOLVATOR ON PVC COMPOUND RAW MATERIAL COST

Compound		A	B
		-Pounds-	
PVC		100	100
DOP		50	40
Fast-Solvating Plasticizer		-	10
Stabilizer/Lubricant		3	3
Total Pounds		153	153
	Sp. Gr.	Pound Volumes	
PVC	1.4	71.43	71.43
DOP	0.986	50.71	40.57
Fast-Solvating Plasticizer	1.12	-	8.93
Stabilizer/Lubricant	1.00	3.00	3.00
Total Pound Volumes		125.14	123.93
	¢/Pound	¢	
PVC	42	4200	4200
DOP	47	2350	1880
Fast-Solvating Plasticizer	50	-	500
Stabilizer/Lubricant	100	300	300
Total¢		6850	6880
Sp. Gr.		1.223	1.235
¢/Pound (Total¢/Total Pounds)		44.77	44.97
¢/Pound Volume (Total¢/Total Pound Volumes)		54.74	55.52
$\$/Ft^3$ 62.3(¢/Pound Volume/100)		34.10	34.59
\$/100 yard roll ($\$/Ft^3$ x 1.35)		46.04	46.70

Added cost/100 yard roll = 46.70 - 46.04 = $0.66.

mixing, fluxing, straining, and calendering energy consumption. Since the one hundred yard roll of 54 inch width 12 mil sheeting equals 1.35 $ft.^3$ and weighs 1.35 x 62.3 x 1.223 = 103 lbs (in the case of Compound A), energy cost would be $2.06. Thus, energy usage would have to be cut by 32 percent just to offset the 66¢ increase in raw materials cost. Energy savings of this magnitude seem unlikely.

In some cases, taking the opposite approach, using slower solvating, higher molecular weight and less efficient phthalates, such as DINP and DIDP, has been shown to increase plant output in certain calendering and extrusion operations. Table II compares results of a wire insulation extrusion study with DOP vs. DINP. It was found that at comparable temperatures and screw speeds, output of the DINP formulation was 17 percent higher on a volume basis than that of the DOP formulation. In this example 58 phr (parts per hundred of resin) of DINP was compared with 55 phr of DOP (equal efficiency levels).

The importance of comparing plasticizers at equal efficiency levels (equal hardness or 100% modulus) rather than equal phr cannot be overemphasized. This is shown in Table III for a typical plastisol compound. It can be seen that use of a less efficient plasticizer, such as DIDP, even though it costs one half cent per pound more than DOP, results in a pound volume cost savings of 0.7¢.

For those who calculate costs on a weight basis the higher cost per pound of the DIDP compound can be more than compensated for by addition of extra filler. For example, as shown in Table III adding an extra 7 phr of $CaCO_3$ and an extra phr of DIDP equates specific gravity to that of the DOP compound. This results in a savings of 1.17 cents per pound or 1.51 cents per pound volume.

The point of the foregoing was to illustrate the importance of considering all aspects of formulation changes - energy savings may or may not be real, and the extra compound cost, plus possible adverse affects on overall performance must also be considered.

5. Other Factors Influencing the Use of Monohydric Alcohol Based PVC Plasticizers in the Eighties. Increasing attention to the cost of fuming losses - especially in calendering and spread coatings and the increasing restrictions on stack emissions and the in-plant environment will tend to continue the trend to less volatile plasticizers - i.e., higher molecular weight phthalates than DOP. Figure 1 shows comparative volatilities of various GP plasticizers(23). It is obvious that DOP volatility during the fusion process is much greater than that of higher dialkyl phthalates. Aside from improving the environment, there is an opportunity then to cut economic losses through selection of lower volatility plasticizers.

The use of hydrocarbon plasticizers as partial replacements for monohydric alcohol phthalates may tend to decrease as a result

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TABLE II

WIRE INSULATION EXTRUSION STUDY

(0.8 mm Wall Thickness)

Plasticizer (phr)	DOP(50)	DINP(58)
Extruder Temperature, °C		
Rear Zone	174	171
Middle Zone	182	183
Front Zone	187	188
Die	190	191
Screw Speed, RPM	118	118
Volume Output, % of DOP	100	117

Formulation

PVC	100
Plasticizer	as shown
Lead Stabilizer	5
$CaCO_3$	10
Calcined Clay	10
Stearic Acid	0.125

TABLE III

ECONOMIC COMPARISON OF DOP VS. DIDP IN PLASTISOL COMPOUNDS

Compound		C	D	E
		-Pounds-		
PVC		100	100	100
DOP		60	-	-
DIDP		-	66	67
Stabilizer		3	3	3
$CaCO_3$		20	20	27
Total Pounds		183	189	197
	Sp. Gr.	Pound Volumes = Pounds/Sp. Gr.		
PVC	1.4	71.43	71.43	71.43
DOP	0.986	60.85	-	-
DIDP	0.968	-	68.18	69.21
Stabilizer	1.00	3.00	3.00	3.00
$CaCO_3$	2.71	7.38	7.38	9.96
Total Pound Volumes		142.66	149.99	153.60
	¢/Pound	¢ = ¢/Pound x Pounds		
PVC	50	5000	5000	5000
DOP	47	2820	-	-
DIDP	47.5	-	3135	3183
Stabilizer	100	300	300	300
$CaCO_3$	5	100	100	135
Total¢		8220	8535	8618
Sp. Gr.		1.283	1.260	1.283
¢/Pound (Total¢/Total Pounds)		44.92	45.16	43.75
¢/Pound Volume (Total¢/Total Pound Volumes)		57.62	56.90	56.11
¢/Pound Volume Savings (vs. DOP)		-	0.72	1.51

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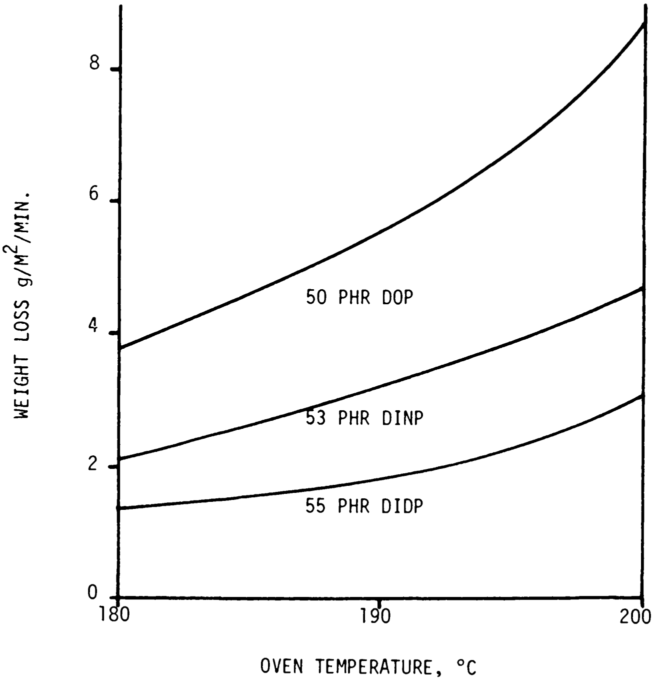

Figure 1. Weight loss from spread coating (Werner–Mathis oven; coating thickness: 0.25 mm; dwell time: 2 min)

again of more restrictive air pollution controls. In addition, there is increasing concern about the toxicity of certain highly aromatic types used, particularly in low cost plastisol formulations. In those cases where hydrocarbon type plasticizers are used, the use of higher molecular weight phthalates, such as DIDP, will overcome to some extent the overall high volatility.

The use of trimellitates is expected to regain ground lost due to TMA shortages in the late seventies. Polymerics will continue to be used in those areas where high solvent extraction resistance and migration are major concerns. Phosphates are expected to continue their growth in flame retardant applications. Also, new capacity for dioctyl terephthalate (DOTP) has been announced(25).

Finally, a recently published draft report of a National Toxicology Program study found DOP (or DEHP as it is referred to in toxicology studies) to be carcinogenic to certain strains of mice and rats when fed at very high levels in the diet for the lifetime of the test animals. It may be a number of years before the mechanism of the induced carcinogenic effects can be understood, and a realistic assessment of any risk to man can be made. The final version of the draft report is expected to issue in February, 1981.

Conclusions

It appears that monohydric alcohol phthalates will continue to dominate the vinyl plasticizer market in the eighties. But, the growth of specific types of alcohols is continuing to change - a trend that started in the fifties and sixties, became a landslide in the seventies, and is expected to continue in the eighties. Increased attention to raw material and energy costs and production rates, will be required for the vinyl fabricator to remain competitive. In addition, the overall impact of formulation changes, aside from economics, must be more carefully weighed, including affect on physical properties, fuming losses, and the environment.

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13

Monohydric Alcohols in the Flavor and Fragrance Industry

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Todays' perfumers and flavorists have a palette of about 5,000 materials at their disposal to formulate the pleasant odors and tasty flavors enjoyed and even demanded in consumer products. Some materials are of natural origin, others are purely synthetic and some are available from both sources, natural and synthetic. Almost all kinds of organic functionalities are represented in the broad palette of the flavorist and perfumer - alcohols, aldehydes, ketones, esters, hydrocarbons, olefins, amines, phenols, heterocyclics, etc. Alcohols are particularly important because they are prominent among the relatively inexpensive and readily available materials which make up the bulk of flavors and especially fragrances.

Flavors vs. Fragrances

Flavors and fragrances are sensory stimuli. Of the two, flavors are more complex because they act on the olfactory bulb via their volatile components and on the taste buds which are stimulated by both volatile and non-volatile components. The overall response to a flavor is a synthesis of the effects of both types of components. The response to fragrances, on the other hand, results only from the action of volatile components. Because flavors and fragrances function via a common mechanism, many volatile materials are used for both purposes. This is nicely illustrated by the perfumers' vocabulary for fragrance materials. A collection of some 160 words published by a famous perfumer, Ernest Shiftan (1) included 75 words usually associated with flavors such as almond, bacon, coconut, honey, lime, raspberry, spicy and vanilla.

Variety and Diversity of Monohydric Alcohols

Givaudan Corporation, probably the largest supplier of flavor and fragrance chemicals, offers about 50 monohydric alcohols. This is by no means the whole picture. Other suppliers offer additional alcohols and some alcohols are used in-house as intermediates,

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RHODINOL	50%
GERANIOL COEUR	5
CITRONELLOL COEUR	10
PHENYLETHYL ALCOHOL COEUR	10
NEROL COEUR	5
GERANYL ACETATE	2
ALDEHYDE C-8 10%	4
ALDEHYDE C-9 10%	4
BENZOPHENONE	3.5
ROSE OXIDE 1%	1
ROSALVA	0.5
ESSENCE OF STYRAX	3
GUAIACWOOD OIL (GUAIOL)	2
TOTAL	100%

Figure 1. Rose base

ALDEHYDES	45.0%
ALCOHOLS*	48.0
ESTERS	4.0
ACETALS	0.4
PHENOL ETHERS	0.7
KETONES	0.3
NITROGEN COMPOUNDS	0.5
RESINS	0.1
OTHERS	1.0

* HYDROXYCITRONELLAL, TERPINEOL, LINALOOL, PHENYLETHYL ALCOHOL, ANISIC ALCOHOL, DIMETHYLBENZYL CARBINOL, CINNAMIC ALCOHOL

Figure 2. Lilac perfume

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or are only sold in fragrance mixtures. The number of monohydric alcohols used by the industry is no doubt greater than 100.

The importance of monohydric alcohols in fragrances is clearly shown in the formula for a rose base in Figure 1 which contains 82.5% monohydric alcohols. The chemistry of some of these alcohols is covered later.

A typical lilac perfume in Figure 2 contains 48% alcohols, all monohydric.

Nature has been very generous in distributing fragrant alcohols among the flowers. Figure 3 lists the number of different alcohols found in four important floral extracts used in perfumery: jasmin, hyacinth, ylang-ylang and tuberose. The number ranges from 31 to 56 and terpenoid alcohols are the most abundant. Concentrations of individual alcohols in essential oils vary widely, from traces to as much as 80%, in the case of santalol in sandalwood oil.

Nor has nature neglected to bless fruits with alcohols which add their special touch to the flavors of fresh fruit. A list of alcohols found in apple and banana extracts is shown in Figure 4. These examples suffice to show how widely distributed alcohols are in natural flavors and fragrances.

Chemical Types

Before the 19th century, perfumers had at their disposal only natural products of plant and animal origin. Today, perfumers work with about 5,000 materials, most of which are produced synthetically. Among the approximately 100 monohydric alcohols used, all chemical types are represented. Several examples of aliphatic alcohols are shown in Figure 5. Nonyl alcohol and 3-octanol are typical fatty alcohols. These alcohols are often found in natural products but are seldom used because of their weak odor.

In contrast, olefinic alcohols have strong odors and are widely used in perfumes, though at relatively low concentrations. Leaf alcohol has a very pleasant leafy, green odor. It is found in many flowers and fruits and is the most important of the olefinic alcohols. Commercial leaf alcohol contains at least 90% of the *cis* isomer.

Typical aromatic alcohols are shown in Figure 6. Phenylethyl alcohol is the most important member of this family. It is the main constituent of French rose and is also present in Otto of rose. Phenylethyl alcohol has a heavy, sweet odor reminiscent of rose petals. It blends well with other floral odors and is widely used in many floral fragrances. Phenylethyl alcohol is one of the chemical pillars of perfumery because, in addition to its fine odor qualities, it is relatively inexpensive and readily available.

Cinnamic alcohol, anisic alcohol and dimethylphenyl ethyl carbinol are other members of the aromatic alcohol family.

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	ALIPHATIC	AROMATIC	TERPENOID	TOTAL
JASMIN	10	4	17	31
HYACINTH	11	12	33	56
YLANG YLANG	10	7	31	48
TUBEROSE	9	4	21	34

Figure 3. Number of alcohols found in natural floral extracts

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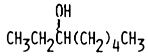
	APPLE	BANANA
1-BUTANOL	X	X
2-BUTANOL		X
ETHANOL	X	X
GERANIOL	X	
1-HEXANOL	X	X
TRANS-2-HEXEN-1-OL	X	
CIS-3-HEXEN-1-OL	X	
METHANOL	X	
2-METHYLBUTAN-1-OL	X	
3-METHYLBUTAN-1-OL	X	X
2-METHYLPROPAN-2-OL	X	X
1-PENTANOL	X	
2-PENTANOL		X
1-PROPANOL	X	X
2-PROPANOL	X	

Figure 4. Alcohols found in fruit extracts

In Monohydric Alcohols; Wickson, E.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1981.

FATTY ALCOHOLS

	ODOR TYPE
$CH_3(CH_2)_7CH_2OH$ NONYL ALCOHOL	FATTY - ORANGE
 3-OCTANOL	PEPPERMINT-SAGE

OLEFINIC ALCOHOLS

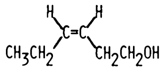
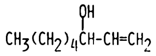
 LEAF ALCOHOL cis-3-HEXENOL	GREEN LEAF
 1-OCTEN-3-OL	MUSHROOM VERY STRONG

Figure 5.

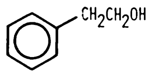
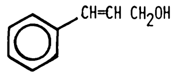
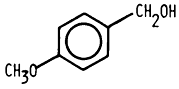
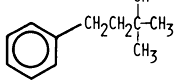
	ODOR TYPE
 PHENYL ETHYL ALCOHOL	ROSE-HONEY
 CINNAMIC ALCOHOL	BALSAMIC-FLORAL
 ANISYL ALCOHOL	FLORAL BALSAMIC
 DIMETHYLPHENYLETHYL CARBINOL	LILY HYACINTH

Figure 6. Aromatic alcohols

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Terpenoid alcohols appeared early in the history of synthetic perfumery because several were readily available from inexpensive essential oils. Alpha-terpineol, citronellol and linalool shown in Figure 7 are important constituents of pine stump oil, citronella oil and rosewood oil, respectively. The fourth material listed, hydroxycitronellal, is a hydroxy aldehyde which perhaps has a questionable place in this discussion. It is included because it is one of the most important fragrance chemicals used today. "Hydroxy" is almost a perfume unto itself. Its soft flowery, linden blossom odor blends very well in many floral perfumes.

Sesquiterpenic alcohols used in perfumery are mainly of natural origin. Three alcohols of this type are shown in Figure 8. Cedrol is the main alcohol constituent of cedarwood oil. Alpha-santalol constitutes about 80% of sandalwood oil and about 30% patchouli alcohol is found in patchouli oil, a very popular woody-earthy fragrance material.

Ethyl Alcohol

Perfumes, colognes and toilet waters are solutions of perfume oils in specially denatured alcohols, (ethyl alcohol with various denaturants which make it unsuitable for human consumption). In addition, ethanol is used as a solvent for flavors, as an extraction solvent for many natural products and as a reagent for the production of many ethyl esters. Summing up all these uses, the quantity of ethanol used in the fragrance and flavor industry tops all other alcohols by far.

Perfumes contain 10-25% oil in SDA 39C. The denaturant is diethyl phthalate - 1:100. Colognes and toilet waters contain 2-6% oil in SDA 40 as shown in Figure 9. The denaturant is brucine sulfate - 3 oz. per 100 gallons. Ethanol used as a solvent for flavors is the 95% grade and is fully taxed since it is potable. All ethanol used for fragrances and flavors must get by the close scrutiny of the Quality Control perfumer or flavorist. The road can be rough.

Hydroxycitronellal

This is probably the single most important material used by the fragrance industry. Several million pounds are used annually, mainly in soaps and detergents. The principal method of manufacture shown in Figure 10 is by hydration of citronellal via the bisulfite addition product (2). The aldehyde moiety must be protected before hydration. A second manufacturing process starts with citronellol which is hydrated under acid conditions. The primary alcohol end of the molecule is then dehydrogenated catalytically or by oxidation to the aldehyde.

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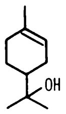
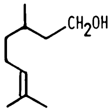
ODOR TYPE



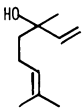
ALPHA-TERPINEOL

LILAC



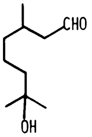
CITRONELLOL

FRESH - ROSEY



LINALOOL

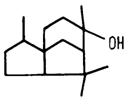
FLORAL - WOODY



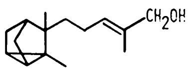
HYDROXYCITRONELLAL

LILY-OF-THE-VALLEY

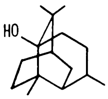
Figure 7. ***"Terpenoid" alcohols***



CEDROL



ALPHA-SANTALOL



PATCHOULI ALCOHOL

Figure 8. ***Sesquiterpenic alcohols***

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PERFUME

10-25% OIL IN 95% 39C ALCOHOL

COLOGNE/TOILET WATER

2-6% OIL IN 60-80% 40 ALCOHOL

Figure 9. Ethyl alcohol

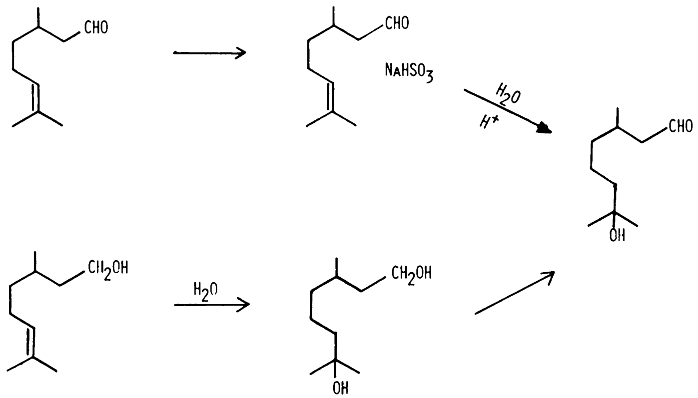

Figure 10. Hydroxycitronellal

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Menthol

Peppermint flavor and "cool" cigarettes owe their distinctive flavor character to 1-menthol, a secondary alcohol and another multimillion-pound product of the industry. Pure 1-menthol is used mainly for flavoring cigarettes and much of this material is isolated from the Mentha arvensis plant. Substantial quantities are also produced synthetically from meta-cresol as shown in Figure 11. Isopropylation yields a mixture of isomers from which thymol is isolated. Hydrogenation of thymol gives a mixture of menthol isomers. Racemic menthol is recovered from the mixture by careful fractionation of menthol as an ester. 1-Menthol is the desired isomer because it is responsible for the cooling effect. Several practical methods have been described for separating the 1-isomer. One patented by Haarmann and Reimer is especially intriguing (3). A supersaturated solution of racemic menthol esters is seeded with the 1-ester which then selectively crystallizes.

Geraniol/Citronellol

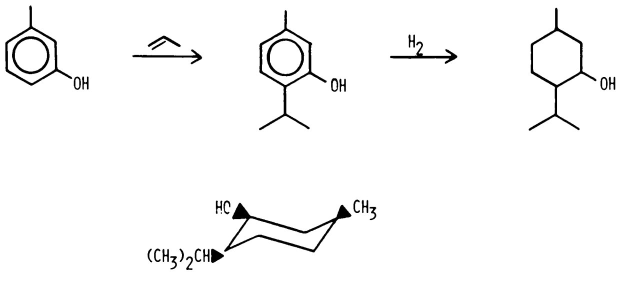
These "rose" alcohols were formerly obtained from citronella oil as a 2:1 mixture of geraniol/citronellol. High purity citronellol was obtained by hydrogenation of the mixture. Soap perfumery was highly dependent on cheap natural geraniol/citronellol. Since the 1960's, synthetic geraniol has been a controlling factor in the market for these alcohols. The synthetic route is shown in Figure 12. Myrcene, produced by pyrolysis of beta-pinene, is converted to a mixture of geraniol and nerol, its cis isomer, first by reaction with HCl, then with sodium acetate and finally with sodium hydroxide to saponify the esters.

Commercialization of this chemistry by Glidden (4) was the first case where synthesis freed the industry from total dependence on a natural source of a major product.

Linalool

In the mid-1950's, Hoffmann La-Roche offered synthetic linalool and its esters to the fragrance industry (5). This was another revolutionary step in the replacement of natural products with synthetics. Linalool was an intermediate in Roche's manufacture of synthetic isophytol for Vitamin E. For several years perfumers were reluctant to use chemically pure synthetic linalool and its esters in place of materials isolated from essential oils. Finally, economics prevailed and today the amount of synthetic linalool and its esters used far exceeds the traditional "linalool rich" essential oils.

Worldwide, in excess of five million pounds of linalool and its esters are manufactured for fragrances by five different processes. Three of them involve methylheptenone as an intermediate. The other two are based on turpentine. The three routes to methylheptenone are outlined in Figure 13.



L-MENTHOL

Figure 11. Menthol

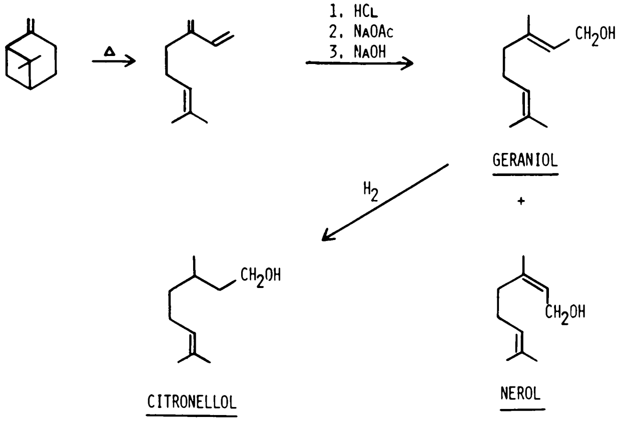


Figure 12. Geraniol/citronellol

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In the first route, methylbutenol is made from acetone and acetylene followed by hydrogenation. Reaction with methyl isopropenyl ether yields methylheptenone (6). The second route involves the reaction of isobutylene, formaldehyde and acetone (7). Methyl vinyl ketone is an intermediate. Finally, methylheptenone is made by alkylation of acetone with prenyl chloride which is derived from isoprene (8). The initial product is the terminal olefin which is isomerized to the desired isopropylidene compound.

As shown in Figure 14, linalool is obtained by ethynylation of methylheptenone, followed by hydrogenation.

Sandalore

Some of the chemistry developed by the industry more recently, to produce new monohydric alcohols, is just as interesting as the linalool chemistry. Sandalore, a recent new Givaudan chemical with a persistent, sandalwood odor is made according to the scheme in Figure 15 (9). Alpha-pinene, the starting material, is converted to the epoxide which is catalytically rearranged to campholenic aldehyde. Aldol condensation with methyl ethyl ketone followed by hydrogenation yields Sandalore®.

Phenylethyl Alcohol

This important fragrance material probably was introduced in commercial perfumery during the first decade of the twentieth century with the discovery of the Bouveault-Blanc reduction of esters by sodium and an alcohol (10). This is the first of several methods of preparation shown in Figure 16. Large quantities of phenylethyl alcohol were made by sodium reduction of butyl phenylacetate in normal butanol. The basic raw materials were readily available at low cost from benzyl chloride, sodium cyanide and fermentation butanol.

This process was superceded by the Friedel-Crafts reaction of benzene and ethylene oxide which is now the most important commercial process (11). Cheap ethylene oxide brought about this shift. For a short time, commercial quantities of phenylethyl alcohol were made by the Grignard reaction of phenyl magnesium chloride on ethylene oxide but this process could not compete with the Friedel-Crafts process.

More recently, low cost styrene oxide has been considered as a starting material. Catalytic hydrogenation under controlled conditions yields high quality phenylethyl alcohol (12). Unfortunately, low cost styrene oxide never matérialized in this country; consequently, little phenylethyl alcohol has been manufactured by this route.

The four methods of producing phenylethyl alcohol depicted in Figure 16 illustrate the dependence of the fragrance industry on the organic chemical industry. Most large volume products used in

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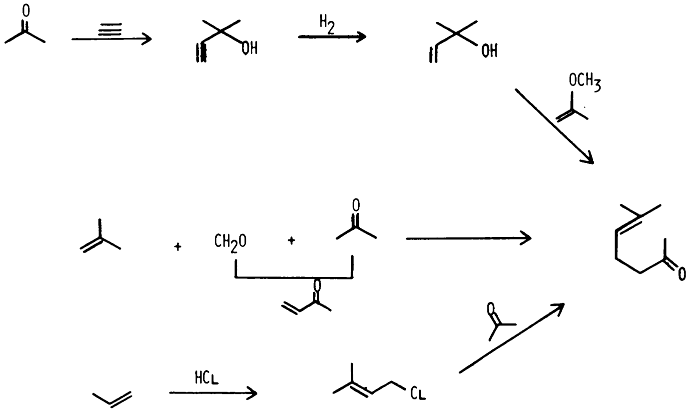

Figure 13. Methylheptenone

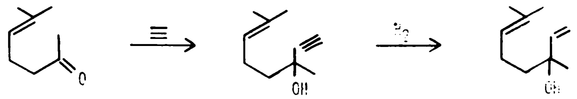

Figure 14. Linalool

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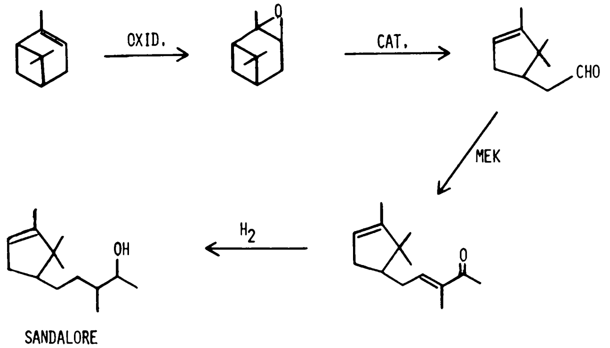

Figure 15. Sandalore

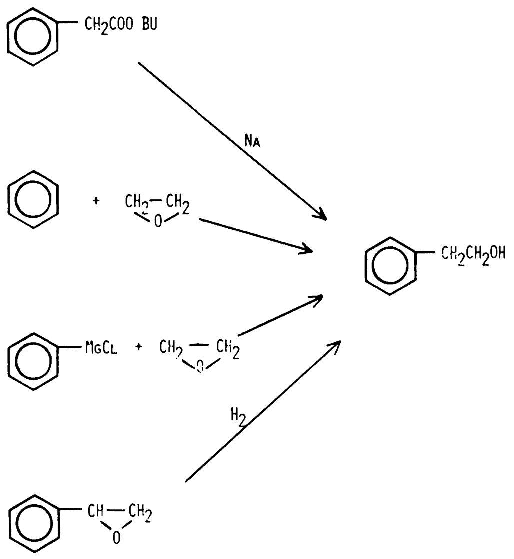

Figure 16. Phenylethyl alcohol

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perfumes are commodity items that must be made by the least expensive process. Very often, raw materials cost determines which process will prevail.

This overview of monohydric alcohols covered the major products used by the industry. The one exception was Sandalore which was introduced only recently. It was included as an example of the continuing search for new fragrance materials to replace natural products,in this case, expensive and scarce sandalwood oil. It is hoped that a similar review in five years would include Sandalore or another major new, synthetic fragrance alcohol.

Abstract

Monohydric alcohols are found in great variety in natural flavor and fragrance materials. Many chemical types are represented: aliphatic, alicyclic, polycyclic, heterocyclic, terpenoid, saturated, unsaturated, etc. In flavor and odor they cover practically the entire useful spectrum. Some are present in low concentrations and others are the principal components of the natural products. Flavorists and perfumers first formulated sophisticated flavors and fragrances using naturally occurring alcohols. As the art and science progressed, chemists devised synthetic routes to many of the important natural alcohols and produced them cheaper and in higher quality. Commercial synthesis of some natural alcohols, such as, geraniol, citronellol, menthol and linalool has had a very significant impact on the economics of the flavor and fragrance industry. The preparation and use of the more important monohydric alcohols is reviewed.

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